

LIST OF FIGURES

| | |
|--|----|
| Figure 1.1 Pictorial view of hopping of cation through polymer chain motion and via ion clusters. | 9 |
| Figure 1.2 Schematic view of polymer host with inorganic nanofiller with the size of nanometre and (b) micron interfaced with electrodes. | 13 |
| Figure 1.3 Schematic diagram of a typical battery. | 14 |
| Figure 1.4 Comparison of all types of batteries in terms of energy density. | 15 |
| Figure 1.5 Schematic structure of Supercapacitor. | 15 |
| Figure 1.6 Classifications of Supercapacitor. | 16 |
| Figure 1.7 Schematic diagram of fuel cell. | 16 |
| Figure 1.8 Schematic representation of Dye-sensitized Solar Cell. | 17 |
| Figure 1.9 Schematic diagram and configuration of electrochromic device design. | 18 |
| Figure 1.10 Schematic diagram of the structure for the blended polymer electrolyte. | 20 |
| Figure 2.1 A percolation pattern, with available fraction of bond which is a pathway for the motion of ions between available sites. | 35 |
| Figure 2.2 Schematic diagram of non-percolation and percolation path for ion transportation in the amorphous and solvent swollen polymer. | 36 |
| Figure 2.3 Space charge layer around nano-sized particles. | 37 |
| Figure 2.4 Schematic diagram of the morphology of composite polyether non-conductive filler electrolytes. | 38 |
| Figure 2.5 A schematic representation of a polymer matrix with a single nanofiller grain dispersion. | 38 |
| Figure 2.6 Schematic of Lewis acid-base interactions between a PEO–LiClO ₄ electrolyte host and a nanoparticle guest. | 39 |
| Figure 2.7 Lubricity theory explaining plasticizers-polymer response. | 40 |
| Figure 2.8 Plasticizer polymer action based on gel theory. | 40 |
| Figure 2.9 Schematic representation of increased free volume upon addition plasticizers. | 41 |
| Figure 2.10 Specific free volume -temperature curve. | 41 |
| Figure 2.11 Set up for four probes method. | 43 |
| Figure 2.12 AC complex impedance plot in the complex plane. | 44 |
| Figure 2.13 Complex impedance plots and equivalent circuits. | 47 |
| Figure 2.14 Complex impedance plot of (a) ideal system (b) real system. | 48 |
| Figure 2.15 (a) A polycrystalline sample sandwiched between electrode (b) Impedance plot of polycrystalline system. | 48 |
| Figure 2.16 Schematic representation of polarisation (a) Electronic or atomic polarization (b) Ionic polarisation (c) Orientation or dipolar polarization (d) Space-charge or interfacial polarisation. | 50 |
| Figure 2.17 Dielectric constant, dielectric loss, and different polarization mechanisms as a function of frequency. | 51 |
| Figure 2.18 Schematic representation of Debye relaxation behavior. | 52 |
| Figure 2.19 Vector diagram of complex dielectric permittivity. | 52 |
| Figure 2.20 Typical AC ionic conductivity plot (log σ' vs. log f) for ionic conductor. | 55 |
| Figure 3.1 Solution cast technique in the form of a flow chart. | 64 |
| Figure 3.2 Flow chart for preparation of gel polymer electrolyte. | 69 |
| Figure 3.3 Photographs of gel polymer electrolyte (GPE) film. | 70 |
| Figure 3.4 Schematic diagram and real view of XRD. | 71 |
| Figure 3.5 Diffraction in crystalline materials having lattice parameter (d). | 72 |
| Figure 3.6 BRUKER D2-Phaser. | 72 |
| Figure 3.7 Modes of vibration. | 74 |
| Figure 3.8 Optical diagram of Fourier transform infrared spectroscopy. | 75 |
| Figure 3.9 Interpretation of Infrared spectra. | 75 |
| Figure 3.10 FTIR 4100 JASCO model. | 75 |
| Figure 3.11 Schematic diagram of the DSC technique. | 77 |
| Figure 3.12 Typical thermograph of thermal analysis. | 77 |
| Figure 3.13 SII EXSTAR 6000 DSC model. | 78 |
| Figure 3.14 Schematic diagram of SEM. | 79 |
| Figure 3.15 JEOL JSM-6010LA SEM Model. | 80 |

| | |
|---|-----|
| Figure 3.16 Block diagram of working of Atomic force microscope (AFM). | 81 |
| Figure 3.17 Easy Scan 2 AFM version 2.0 Nanosurf. | 81 |
| Figure 3.18 Experimental arrangement for Wagner's polarization method. | 83 |
| Figure 3.19 Typical DC polarization current versus time. | 83 |
| Figure 3.20 Signal applied in cyclic voltammetry: Potential as a function of time. | 86 |
| Figure 3.21 A typical I-V plot of cyclic voltammetry experiment. | 86 |
| Figure 3.22 Solartron 1287 electrochemical interface with 1260 impedance gain phase analyzer. | 86 |
| Figure 3.23 A typical stress-strain curve. | 87 |
| Figure 3.24 Mechanical tester (Model 5848, Singapore). | 88 |
| Figure 3.25 (a) A sample with an AC signal applied across it (b) A typical complex impedance plot. | 89 |
| Figure 3.26 (a) Solartron SI-1260 Impedance Gain/Phase Analyser interfaced with computer (b) Sample holder. | 90 |
| Figure 4.1 XRD pattern of pure PVDF-HFP and PMMA. | 96 |
| Figure 4.2 XRD pattern of LiClO_4 . | 96 |
| Figure 4.3 XRD pattern of GPE system with different concentrations of LiClO_4 - Series (a). | 96 |
| Figure 4.4 XRD pattern of GPE system with different concentrations of PC:DEC - Series (b). | 97 |
| Figure 4.5 XRD analysis of GPE with various amount of Al_2O_3 nano-filler - Series (c). | 98 |
| Figure 4.6 SEM micrographs of GPE system with different concentrations of LiClO_4 - Series (a). | 100 |
| Figure 4.7 SEM micrographs of GPE system with different concentrations of PC:DEC - Series (b). | 101 |
| Figure 4.8 SEM micrographs of nanocomposite GPE system with different concentrations of Al_2O_3 - Series (c). | 102 |
| Figure 4.9 DSC thermogram of (a) pure PVDF-HFP (b) pure PMMA (c) PVDF-HFP:PMMA blend. | 104 |
| Figure 4.10 DSC thermograph of GPE system with different concentrations of LiClO_4 - Series (a). | 105 |
| Figure 4.11 DSC thermograph of GPE system with different concentrations of PC:DEC - Series (b). | 106 |
| Figure 4.12 DSC thermograph of nanocomposite GPE system with different concentration of Al_2O_3 - Series (c). | 107 |
| Figure 4.13 FTIR spectra of pure PVDF-HFP, pure PMMA, LiClO_4 , PC, and DEC. | 108 |
| Figure 4.14 FTIR spectra of GPE with different concentrations of LiClO_4 - Series (a). | 110 |
| Figure 4.15 FTIR spectra of GPE with different concentrations of PC:DEC - Series (b). | 111 |
| Figure 4.16 FTIR spectra of nanocomposite GPE with different concentrations of Al_2O_3 -Series (c). | 113 |
| Figure 4.17 AFM images of GPE having (a) 7.5 wt.% and (b) 10 wt.% LiClO_4 - Series (a). | 114 |
| Figure 4.18 AFM images of GPE having (a) 30 wt.% and (b) 60 wt.% PC:DEC - Series (b). | 114 |
| Figure 4.19 AFM images of GPE having (a) 0.5 wt.% and (b) 2 wt.% Al_2O_3 - Series (c). | 115 |
| Figure 4.20 Cyclic voltammogram of GPE having 4 wt.% and 7.5 wt.% LiClO_4 - Series (a). | 117 |
| Figure 4.21 Cyclic Voltammogram of GPE having 40 wt.% and 60 wt.% PC:DEC - Series (b). | 118 |
| Figure 4.22 Cyclic voltammogram of nanocomposite GPE having 1 wt.% and 2 wt.% Al_2O_3 - Series (c). | 119 |
| Figure 4.23 Stress-strain curve of GPE with different concentrations of LiClO_4 -Series (a). | 120 |
| Figure 4.24 Stress-strain curve of GPE with different concentrations of PC:DEC - Series (b). | 120 |
| Figure 4.25 Stress-strain curve of nanocomposite GPE with different concentrations of Al_2O_3 -Series (c). | 121 |
| Figure 5.1 Residuals plots obtained from Kramers- Kronig relationship for GPE containing (a) 4 wt.% LiClO_4 (b) 7.5 wt.% LiClO_4 - Series (a). | 131 |
| Figure 5.2 Residuals plot obtained from Kramers-Kronig relationship for GPE containing (a) 40 wt.% PC:DEC (b) 60 wt.% PC:DEC -Series (b). | 132 |
| Figure 5.3 Residual plot obtained from Kramer-Kronig relationship for NCGPE containing (a) 3 wt.% Al_2O_3 (b) 4 wt.% Al_2O_3 - Series (c). | 132 |
| Figure 5.4 The complex impedance plot for different concentrations of LiClO_4 in the GPE system at different temperatures - Series (a). | 133 |
| Figure 5.5 (a) The complex impedance plot for different concentrations of LiClO_4 in the GPE system at 303 K (b) Equivalent circuit fitting of impedance plot of GPE with 4 wt.% LiClO_4 at 303 K - Series(a). | 134 |
| Figure 5.6 Variation of ionic conductivity as a function of LiClO_4 salt concentration at 303 K- Series (a). | 135 |
| Figure 5.7 The complex impedance plot for different concentrations of PC:DEC in the GPE system at different temperatures - Series(b). | 136 |
| Figure 5.8 (a)The complex impedance plot for different concentrations of PC: DEC plasticizers in the GPE system at 303 K (b) Equivalent circuit fitting of the impedance plot of GPE with 40 wt.% PC:DEC at 303 K - Series (b). | 137 |

| | |
|--|-----|
| Figure 5.9 Variation of ionic conductivity as a function of PC:DEC plasticizers concentration at 303 K - Series(b). | 138 |
| Figure 5.10 The complex impedance plot for different concentrations of Al_2O_3 in the GPE system at different temperatures – Series (c). | 140 |
| Figure 5.11 (a) The complex impedance plot for different concentrations of Al_2O_3 nano-particles in the GPE system at 303 K (b) Equivalent circuit fitting of the impedance plot of GPE containing 1 wt.% Al_2O_3 at 303 K - Series (c). | 141 |
| Figure 5.12 Variation of ionic conductivity as a function of Al_2O_3 concentration at 303 K - Series(c). | 141 |
| Figure 5.13 (a)Temperature dependence of ionic conductivity ($\log \sigma_{dc}$ versus $1000/T$) of GPE with different concentrations of LiClO_4 . (b) Variation of ionic conductivity and activation energy as a function of LiClO_4 salt concentration – Series (a). | 142 |
| Figure 5.14 (a) Temperature dependence of ionic conductivity ($\log \sigma_{dc}$ versus $1000/T$) of GPE with different concentrations of PC: DEC. (b) Variation of ionic conductivity and activation energy as a function of PC: DEC concentration - Series (b). | 143 |
| Figure 5.15 (a) Temperature dependence of ionic conductivity ($\log \sigma_{dc}$ versus $1000/T$) of GPE with different concentrations of Al_2O_3 . (b) Variation of ionic conductivity and activation energy as a function of Al_2O_3 concentration - Series(c). | 145 |
| Figure 5.16 Variation of AC conductivity as a function of frequency ($\log \sigma'$ versus $\log f$) for different concentrations of LiClO_4 in the GPE system at different temperatures – Series (a). | 147 |
| Figure 5.17 Variation of AC conductivity as a function of frequency ($\log \sigma'$ versus $\log f$) of GPE systems with different concentrations of LiClO_4 at 303 K - Series (a). | 148 |
| Figure 5.18 (a) $\log \omega_p$ versus $1000/T$ for different concentrations of LiClO_4 in the GPE system. (b) Variation of hopping frequency as a function of LiClO_4 concentration at 303 K – Series (a). | 151 |
| Figure 5.19 Variation of mobile ion factor K as a function of the temperature of GPE with different LiClO_4 content (inset: Variation of K with LiClO_4 content at 303 K) – Series (a). | 151 |
| Figure 5.20 Frequency exponent as a function of temperature for all GPE system with different LiClO_4 concentration – Series (a). | 152 |
| Figure 5.21 Variation of AC conductivity as a function of frequency ($\log \sigma'$ versus $\log f$) for different concentrations of PC: DEC in the GPE system at different temperatures - Series (b). | 153 |
| Figure 5.22 Variation in AC conductivity as a function of frequency ($\log \sigma'$ versus $\log f$) of GPE system with different concentrations of PC: DEC at 303 K - Series (b). | 154 |
| Figure 5.23 (a) $\log \omega_p$ versus $1000/T$ for different concentrations of PC: DEC in the GPE system (b) Variation of hopping frequency as a function of PC: DEC concentration at 303 K - Series(b). | 156 |
| Figure 5.24 Variation of mobile ion factor K as a function of the temperature of GPE with different PC: DEC content. (inset: Variation of K with PC: DEC content at 303K) – Series (b). | 156 |
| Figure 5.25 Frequency exponent as a function of temperature for all GPE system with different PC: DEC concentrations – Series (b). | 156 |
| Figure 5.26 Variation of AC conductivity as a function of frequency ($\log \sigma'$ versus $\log f$) for different concentrations of Al_2O_3 in the GPE system at different temperatures – Series (c). | 158 |
| Figure 5.27 Variation of AC conductivity as a function of frequency ($\log \sigma'$ versus $\log f$) of GPE system with different concentrations of Al_2O_3 at 303 K – Series (c). | 159 |
| Figure 5.28 (a) $\log \omega_p$ versus $1000/T$ for different concentrations of Al_2O_3 nanofiller in the GPE system. (b) Variation of hopping frequency as a function of Al_2O_3 nanofiller at 303 K – Series (c). | 159 |
| Figure 5.29 Variation of mobile ion factor K as a function of the temperature of NCGPE with different Al_2O_3 content (inset: Variation of K with Al_2O_3 content at 303 K – Series (c). | 159 |
| Figure 5.30 Frequency exponent as a function of temperature for all NCGPE system with different Al_2O_3 concentration – Series (c). | 160 |
| Figure 5.31 Scaled conductivity spectra for different concentrations of LiClO_4 in the GPE system at different temperatures (using Eq. 5.15) – Series (a). | 161 |
| Figure 5.32 Scaled conductivity spectra for different concentrations of LiClO_4 in the GPE system at different temperatures (Using Eq. 5.17) – Series (a). | 163 |
| Figure 5.33 AC conductivity scaling spectrum of GPE containing different concentrations of LiClO_4 at 303 K (Using Eq. 5.17) – Series (a). | 164 |
| Figure 5.34 Scaled conductivity spectra for different concentrations of PC: DEC in the GPE system at different temperatures (using Eq. (5.15) – Series (b). | 165 |

| | |
|--|-----|
| Figure 5.35 Scaled conductivity spectra for different concentrations of PC: DEC in the GPE system at different temperatures (Using Eq. 5.17) – Series (b). | 166 |
| Figure 5.36 AC conductivity scaling spectrum of GPE containing different concentration PC: DEC at 303 K (Using Eq. 5.17) – Series (b). | 166 |
| Figure 5.37 Scaled conductivity spectra for different concentrations of Al_2O_3 in the GPE system at different temperatures (using Eq. 5.15) – Series (c). | 167 |
| Figure 5.38 Scaled conductivity spectra for different concentrations of Al_2O_3 in the GPE system at different temperatures (Using Eq. 5.17) – Series (c). | 168 |
| Figure 5.39 AC conductivity scaling spectrum of GPE containing different concentrations of Al_2O_3 at 303 K (Using Eq. 5.17) – Series (c). | 169 |
| Figure 5.40 Dielectric constant (ϵ') as a function of frequency for different concentrations of LiClO_4 in the GPE system at different temperatures – Series (a). | 171 |
| Figure 5.41 Temperature dependent dielectric constant (ϵ') at different frequencies for GPE containing (a) 4 wt.% LiClO_4 (b) 7.5 wt.% LiClO_4 – Series (a). | 172 |
| Figure 5.42 (a) Dielectric constant (ϵ') versus $\log f$ for different concentrations of LiClO_4 salt in the GPE system at 303 K. (b) Variation of ϵ' as a function of LiClO_4 concentrations at different frequencies at 303 K – Series (a). | 173 |
| Figure 5.43 Dielectric constant (ϵ') as a function of frequency for different concentrations of PC: DEC in the GPE system at different temperatures – Series (b). | 174 |
| Figure 5.44 Temperature dependent dielectric constant (ϵ') at different frequencies for GPE containing (a) 40 wt.% PC:DEC (b) 60 wt.% PC:DEC – Series (b). | 174 |
| Figure 5.45 (a) Dielectric constant (ϵ') versus $\log f$ for different concentrations of PC:DEC in the GPE system at 303 K. (b) Variation in ϵ' as a function of PC: DEC concentration at different frequencies at 303 K – Series (b). | 174 |
| Figure 5.46 Dielectric constant (ϵ') as a function of frequency for different concentrations of Al_2O_3 in the GPE system at different temperatures – Series (c). | 177 |
| Figure 5.47 Temperature dependent dielectric constant (ϵ') at different frequencies for NCGPE containing (a) 2 wt.% Al_2O_3 (b) 4 wt.% Al_2O_3 – Series (c). | 177 |
| Figure 5.48 (a) Dielectric constant (ϵ') versus $\log f$ for different concentrations of Al_2O_3 nano-filler in the GPE system at 303 K (b) Variations in ϵ' as a function of Al_2O_3 concentration at different frequencies at 303 K – Series (c). | 178 |
| Figure 5.49 Variation of loss tangent ($\tan\delta$) versus $\log f$ for different concentrations of LiClO_4 salt in the GPE system at different temperatures – Series (a). | 179 |
| Figure 5.50 Variation of loss tangent ($\tan\delta$) versus $\log f$ for different concentrations of LiClO_4 salt in the GPE system at 303 K – Series (a). | 180 |
| Figure 5.51 Variation of loss tangent ($\tan\delta$) versus $\log f$ for different concentrations of PC: DEC at different temperatures – Series (b). | 181 |
| Figure 5.52 Variation of loss tangent ($\tan\delta$) versus $\log f$ for different concentrations of PC: DEC in the GPE system at 303 K – Series (b). | 181 |
| Figure 5.53 Variation of loss tangent ($\tan\delta$) versus $\log f$ for different concentrations of Al_2O_3 in the GPE system at different temperatures – Series (c). | 183 |
| Figure 5.54 Variation of loss tangent ($\tan\delta$) versus $\log f$ for different concentrations of Al_2O_3 in the GPE system at 303 K – Series (c). | 184 |
| Figure 5.55 Scaled spectra of tangent loss for GPE with 4 wt.% and 5 wt.% LiClO_4 (Series a), 40 wt.%, and 50 wt.% PC: DEC (Series b), NCGPE with 1 wt.% and 3 wt.% Al_2O_3 (Series c). | 185 |
| Figure 5.56 Variations in the imaginary part of modulus (M'') versus $\log f$ for different concentrations of LiClO_4 salt in the GPE system at different temperatures – Series (a). | 187 |
| Figure 5.57 (a) M'' versus $\log f$ for different concentrations of LiClO_4 in the GPE system at 303 K (b) Variation of conductivity relaxation time and DC conductivity as a function of LiClO_4 concentration at 303 K – Series (a). | 188 |
| Figure 5.58 Variations in the imaginary part of modulus (M'') versus $\log f$ for different concentration of PC:DEC in the GPE system at different temperatures – Series (b). | 191 |

| | |
|---|-----|
| Figure 5.59 (a) M'' versus $\log f$ for different concentrations of PC:DEC in the GPE system at 303 K (b) Variation of conductivity relaxation time and DC conductivity as a function of PC:DEC concentration at 303 K – Series (b). | 192 |
| Figure 5.60 Variation in the imaginary part of modulus (M'') versus $\log f$ for different concentrations of Al_2O_3 in the GPE system at different temperatures – Series (c). | 194 |
| Figure 5.61 (a) M'' versus $\log f$ for different concentrations of Al_2O_3 in the GPE system at 303 K (b) Variation of conductivity relaxation time and DC conductivity as a function of Al_2O_3 concentration at 303 K – Series (c). | 195 |
| Figure 5.62 Spectroscopic plot (Z'' and M'' versus $\log f$) for different concentrations of $LiClO_4$ salt in the GPE system at 308 K – Series (a). | 197 |
| Figure 5.63 Spectroscopic plot (Z'' and M'' versus $\log f$) for different concentrations of PC:DEC in the GPE system at 313 K – Series (b). | 198 |
| Figure 5.64 Spectroscopic plot (Z'' and M'' versus $\log f$) for different concentrations of Al_2O_3 in the GPE system 308 K – Series (c). | 199 |
| Figure 5.65 Scaled M'' spectra for GPE with 4 wt.% and 5 wt.% $LiClO_4$ at different temperatures – Series (a). | 200 |
| Figure 5.66 Scaled M'' spectra for GPE containing 40 wt.% and 50 wt.% PC:DEC at different temperatures – Series (b). | 201 |
| Figure 5.67 Scaled M'' spectra for NCGPE containing 0.5 wt.% and 3 wt.% Al_2O_3 at different temperatures – Series (c). | 201 |
| Figure 6.1 The construction diagram of battery. | 211 |
| Figure 6.2 Typical discharge profile of battery. | 212 |
| Figure 6.3 Schematic diagram or cross-sectional view of the fabricated battery. | 215 |
| Figure 6.4 Discharge circuit for testing a cell via a constant load. | 215 |
| Figure 6.5 Discharge profile of cell 1 at 4.8 K Ω , 10 K Ω , and 21 K Ω . | 216 |
| Figure 6.6 Discharge profile of cell 2 at 4.8 K Ω , 10 K Ω , and 21 K Ω . | 217 |
| Figure 6.7 Discharge profile of cell 3 at 4.8 K Ω , 10 K Ω , and 21 K Ω . | 218 |