

LIST OF FIGURES

Figure 2.2: Disorganized (a) and organized (b) models of an amorphous polymer electrolyte	12
Figure 2.3: Thermal dependency of conductivity for PEO –LiTfSI- Calix6P systems	19
Figure 3.1: (a) Structure of calix4 arene molecule and (b) structure of calix6 arene molecule	22
Figure 3.2: Flow diagram for the preparation process of PEO-LiI electrolyte systems.	23
Figure 3.3: Flow diagram for the preparation process of PEO +LiI + inorganic salt Al ₂ O ₃	25
Figure 3.4: Schematic presentation of highly concentrated composite solid polymer electrolytes	25
Figure 3.5: Flow diagram for the preparation process of PEO-LiI – Calix	27
Figure 3.6: FT-IR spectra of PEO membranes doped with calix arenes	28
Figure 3.7: XRD diffractogram for pure PEO, PEO-LiClO ₄ , and different weight percentages of SO ₄ ²⁻	31
Figure 3.8: Arrhenius plot of the PEO:LiClO ₄ -CeO ₂ at different weight percentages at different temperatures	34
Figure 3.9: The Cole-Cole plots of PEO +LiClO ₄ + CeO ₂	35
Figure 4.1: A segment of a polyethylene oxide chain	37
Figure 4.2 : FTIR spectra of pure PEO, and LiI ; (a) PEO- 4wt.% LiI, (b) PEO- 6wt.% LiI, (c) PEO- 8wt.% LiI (d) PEO-10wt.% LiI, (e) PEO-12wt.% LiI and (f) PEO-14wt.% LiI.	39

Figure 4.3: Changes in the peak position of the CH ₂ band on addition of different weight percentage of LiI	41
Figure 4.4: Full Width at Half Maximum (FWHM) for the peak 1332 cm ⁻¹ at different LiI concentration	42
Figure 4.5: FTIR spectra of PEO, LiI and PEO with LiI (a) 96wt.% PEO : 4wt% LiI, (b) 94 wt.% PEO : 6 wt.% LiI, (c) 92 wt.% PEO : 8 wt.% LiI, (d)90 wt.% PEO : 10 wt.% LiI, (e) 88 wt.% PEO: 12wt.% LiI, (f) 86wt.% PEO : 14wt.% LiI	43
Figure 4.6: Full Width at Half Maximum for the peak 1279 cm ⁻¹ at different LiI content	44
Figure 4.7: Changes in the peak position of the LiI band on addition of different weight percentage of LiI	45
Figure 4.8: Schematic representation of Li ⁺ I ⁻	46
Figure 4.9: Deconvoluted iodide peak.	49
Figure 4.10: Percentage of free ions for different wt% of LiI	50
Figure 4.11: PEO, LiI, Al ₂ O ₃ and PEO-LiI-Al ₂ O ₃ . (5-25wt%) (a) 85.5wt. % PEO:9.5wt.% LiI:5wt. % Al ₂ O ₃ , (b) 81.0 wt.% PEO: 9wt.% LiI:10wt.% Al ₂ O ₃ , (c) 76.5wt.% PEO :8.5wt.% LiI:15 wt.% Al ₂ O ₃ , (d) 72.0wt. % PEO : 8wt.% LiI:20wt.% Al ₂ O ₃ , (e) 67.5wt.% PEO : 7.5wt.% LiI : 25wt.% Al ₂ O ₃	53
Figure 4.12: LiI, PEO, Al ₂ O ₃ and PEO-LiI-Al ₂ O ₃ . (5-25wt%) (a) 85.5 wt.% PEO:9.5wt.% LiI:5wt. % Al ₂ O ₃ , (b) 81.0wt.% PEO: 9% wt.LiI:10wt.% Al ₂ O ₃ , (c) 76.5wt.% PEO :8.5wt.% LiI:15wt. % Al ₂ O ₃ , (d) 72 .0 wt.% PEO : 8wt.% LiI:20wt.% Al ₂ O ₃ , (e) 67.5wt.% PEO : 7.5wt.% LiI : 25wt.% Al ₂ O ₃	55
Figure 4.13: FWHM for peak at 1279 cm ⁻¹	56
Figure 4.14: Changes in the peak position of the LiI band on addition of different weight percentage of Al ₂ O ₃	57
Figure 4.17: Percentage of free ions and contact ions for different wt% of Al ₂ O ₃	58
Figure 4.18 : Deconvoluted peak for 1640 cm ⁻¹	

for PEO-LiI- Al ₂ O ₃ system.	61
Figure 4.19: FTIR spectra of Calix 4 and PEO –LiI –calix 4(1%- 5%); (a)89.1wt.% PEO : 9.9 wt.% LiI : 1 wt.% Calix 4, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 4, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3wt.% Calix 4, (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix 4, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix 4	63
Figure 4.20: LiI peak upon addition of different wt% of calix4	64
Figure 4.21: Deconvoluted LiI peak for PEO-LiI- Calix4 system.	66
Figure 4.22: FTIR spectra of Calix 4 and PEO –LiI –calix 4(1%- 5%); (a)89.1 wt.% PEO : 9.9 wt.% LiI : 1wt.% Calix 4, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 4, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 4, (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix 4, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix 4	67
Figure4.23:FWHM for peak 1278 cm ⁻¹ in the PEO-LiI-Calix4 system.	68
Figure 4.24: FTIR spectra of Calix4 and PEO –LiI –calix 4(1%- 5%); (a)89.1wt.% PEO : 9.9 wt.% LiI : 1 wt.% Calix 4, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 4, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 4, (d) 86.4 wt.% PEO : 9.6wt.% LiI : 4 wt.% Calix 4, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5wt.% Calix 4	69
Figure4.25:Deconvoluted peak for 1640 cm ⁻¹ for PEO-LiI- Calix6 system	71
Figure4.26:The % free ions and contact ions in the PEO-LiI-Calix system	72
Figure 4.27: FTIR spectra of Calix 6 and PEO –LiI –calix 6(1%- 5%); (a)89.1wt.% PEO : 9.9 wt.% LiI : 1wt.% Calix 6, (b) 88.2wt.% PEO : 9.8wt.% LiI : 2 wt.% Calix 6, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 6, (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix6, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix6	73
Figure 4.28: FTIR spectra of Calix6 and PEO –LiI –calix 6(1%- 5%); (a)89.1 wt.% PEO : 9.9 wt.% LiI : 1 wt.% Calix 6, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 6,	

(c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 6, (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix6, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix6	74
Figure 4.29: The FWHM for peak at 1279 cm^{-1}	75
Figure 4.30: FTIR spectra of Calix 6 and PEO –LiI –calix 6(1%- 5%); (a)89.1wt.% PEO : 9.9wt.% LiI : 1wt.% Calix 6, (b) 88.2wt.% PEO : 9.8wt.% LiI : 2wt.% Calix 6, (c) 87.3wt.% PEO : 9.7wt.% LiI :3wt.% Calix6, (d) 86.4wt.% PEO : 9.6wt.% LiI : 4wt.% Calix6, (e) 85.5wt.% PEO : 9.5wt.% LiI : 5wt.% Calix6	76
Figure 4.31: A diagram illustrating the various types of the activity of the active filler against the anions of the polymeric electrolyte	77
Figure 4.32 : The possible anion trapping in calix4 arenes	78
Figure 4.33: The possible anion trapping in calix6 arenes	79
Figure 4.34: Pictorial representation of anion trapping in calix arenes	79
Figure 5.1: XRD patterns of pure PEO film and PEO with different wt.% of LiI (a) PEO- 4wt.% LiI, (b) PEO- 6wt.% LiI, (c) PEO- 8wt.% LiI (d) PEO-10wt.% LiI, (e) PEO-12wt.% LiI and (f) PEO-14wt.% LiI	82
Figure 5.2: XRD patterns of pure PEO film and PEO with different wt.:% of LiI. (a) PEO- 4% LiI, (b) PEO- 6% LiI, (c) PEO- 8% LiI (d) PEO-10% LiI, (e) PEO-12% LiI and (f) PEO-14% LiI	86
Figure 5.3: Shows the % of crystallinity of LiI (4 wt.%-14 wt.%) at peak 19°	87
Figure 5.4: Percentage of crystallinity of LiI (4wt.%-14wt.%)at $2\theta=23^{\circ}$	88

- Figure 5.5: XRD pure Al₂O₃ and PEO-LiI-Al₂O₃,
 (a) 85.5wt.% PEO: 9.5wt.% LiI: 5 wt.% Al₂O₃,
 (b) 81.0wt.% PEO: 9wt.% LiI: 10wt.% Al₂O₃,
 (c) 76.5wt.% PEO : 8.5wt.% LiI: 15 wt.% Al₂O₃,
 (d) 72 .0wt. % PEO : 8wt.% LiI: 20wt.% Al₂O₃,
 (e) 67.5 wt.% PEO : 7.5 wt.% LiI : 25 wt.% Al₂O₃ 89
- Figure 5.6: Deconvoluted patterns for pure Al₂O₃ and PEO-LiI-Al₂O₃.
 (5-25 wt %) wt (a) 85.5 wt.% PEO: 9.5wt.% LiI: 5 wt.% Al₂O₃,
 (b) 81.0 wt.% PEO: 9 wt.% LiI: 10 wt.% Al₂O₃,
 (c) 76.5 wt.% PEO : 8.5 wt.% LiI: 15 wt.% Al₂O₃,
 (d) 72 .0 wt. % PEO : 8 wt.% LiI: 20 wt.% Al₂O₃,
 (e) 67.5 wt.% PEO : 7.5 wt.% LiI : 25 wt.% Al₂O₃ 91
- Figure 5.7: Percentage crystallinity of PEO-LiI with
 different wt. % of Al₂O₃ 92
- Figure; 5.8: XRD patterns for Calix 4 and PEO:LiI:Calix 4(1-5 wt.%)
 (a) 89.0wt.% PEO : 10wt.% LiI : 1wt.% Calix 4,
 (b) 88.0wt.% PEO : 10wt.% LiI : 2wt.% Calix 4,
 (c) 87.0wt.% PEO : 10wt.% LiI : 3wt.% Calix 4,
 (d) 86.0wt.% PEO : 10wt.% LiI : 4 wt.% Calix 4,
 (e) 85.0wt.% PEO : 10 wt.% LiI : 5 wt.% Calix 4 94
- Figure 5.9: XRD patterns for Calix6 and PEO:LiI:Calix6 (1-5wt.%)
 (a) 89.0wt.% PEO : 10wt.% LiI : 1wt.% Calix 6,
 (b) 88.0wt.% PEO : 10wt.% LiI : 2wt.% Calix 6,
 (c) 87.0 wt.% PEO : 10wt.% LiI : 3 wt.% Calix 6,
 (d) 86.0wt.% PEO : 10 wt.% LiI : 4wt.% Calix 6,
 (e) 85.0wt.% PEO : 10wt.% LiI : 5wt.% Calix 6 95
- Figure 5.10: Deconvoluted patterns for Calix4 and PEO:LiI:Calix4 (1-5%)
 (a) 89.0% PEO : 10% LiI : 1% Calix 4,
 (b) 88.0% PEO : 10% LiI : 2% Calix 4,
 (c) 87.0% PEO : 10% LiI : 3% Calix 4,
 (d) 86.0% PEO : 10% LiI : 4% Calix 4,
 (e) 85.0% PEO : 10% LiI : 5% Calix 4 96
- Figure 5.11: Deconvoluted patterns for Calix6 and PEO:LiI:Calix6 (1-5 wt.%)
 (a) 89.0wt.% PEO : 10 wt.% LiI : 1wt.% Calix6,
 (b) 88.0wt.% PEO : 10wt.% LiI : 2wt.% Calix 6,
 (c) 87.0wt.% PEO : 10wt.% LiI : 3wt.% Calix 6,
 (d) 86.0wt.% PEO : 10wt.% LiI : 4wt.% Calix 6,
 (e) 85.0wt.% PEO : 10wt.% LiI : 5 wt.% Calix6. 99

Figure 5.12: Percentage crystallinity of Calix4 and Calix6, 1-5 wt. %	100
Figure 6.1: Impedance plot of PEO at room temperature	104
Figure 6.2 (a): Impedance plot of 96 wt.% PEO:4 wt.% LiI at room temperature	104
Figure 6.2 (b): Impedance plot of 94 wt.% PEO: 6 wt.% LiI at room temperature	105
Figure 6.2 (c): Impedance plot of 92 wt.% PEO: 8wt.% LiI at room temperature	105
Figure 6.2(d): Impedance plot of 90 wt.% PEO:10 wt.% LiI at room temperature	106
Figure 6.2(e): Impedance plot of 88 wt.% PEO: 12 wt.% LiI at room temperature	106
Figure 6.2(f): Impedance plot of 86 wt.% PEO-14 wt.% LiI at room temperature	107
Figure 6.3: The conductivity variation of different wt. % of LiI at room temperature	108
Figure 6.4(a) : Impedance plot of PEO: LiI ; 96 wt.% 4 wt.% at 70 ⁰ C temperature	109
Figure 6.4(b): Impedance plot of PEO:LiI; 94 wt.%: 6 wt.% at 70 ⁰ C temperature	109
Figure 6.4(c): Impedance plot of (c) PEO:LiI, 94 wt.%: 8 wt.% at 70 ⁰ C temperature	110
Figure 6.4(d): Impedance plot of PEO:LiI ; 92 wt.%: 10 wt.% at 70 ⁰ C temperature	110

Figure 6.4(e): Impedance plot of PEO:LiI; 88 wt. % : 12 wt. % at 70 ⁰ C	111
Figure 6.4(f): Impedance plot of 86 wt. % PEO-14 wt. % LiI at 70° C	111
Figure 6.5(a): Impedance plot of PEO : LiI; 96 wt. % : 4 wt. % at 100 ⁰ C	112
Figure 6.5(b): Impedance plot of PEO:LiI ; 94 wt. % : 6 wt. % at 100 ⁰ C	112
Figure 6.5(c): Impedance plot of PEO : LiI; 92:8 wt% at 100 ⁰ C	113
Figure 6.5(d): Impedance plot of PEO:LiI; 90:10 wt. % at 100 ⁰ C	113
Figure 6.5(e): Impedance plot of PEO:LiI; 88:12 wt. % at 100 ⁰ C	114
Figure 6.5(f): Impedance plot of PEO : LiI; 86:14 wt. % at 100 ⁰ C	114
Figure 6.6(a): Plot for log σ vs 1000/T for PEO- LiI 96 wt. % : 4 wt. %	115
Figure 6.6(b) : Plot for log σ vs 1000/T for PEO- LiI 94 wt. % : 6 wt. %	116
Figure 6.6(c): Plot for log σ vs 1000/T for PEO- LiI 92 wt. % : 8 wt. %	116
Figure 6.6(d): Plot for log σ vs 1000/T for PEO- LiI 90 wt. % : 10 wt. %	117
Figure 6.6(e): Plot for log σ vs 1000/T for PEO- LiI 88 wt. % : 12 wt. %	118
Figure 6.6(f): Plot for log σ vs 1000/T for PEO-LiI 86 wt. % : 14 wt. %	118
Figure 6.7 (a) : 76.5.0% PEO : 8.5% LiI : 15 % Al ₂ O ₃ at room temperature	120
Figure 6.7 (b): 76.5% PEO : 8.5 % LiI : 15 % Al ₂ O ₃ at 70 ⁰ C.	121
Figure 6.7 (c): 76 .5 % PEO : 8.5 % LiI : 15% Al ₂ O ₃ at 100 ⁰ C	121

Figure 6.8(a): Plot of $\log \sigma$ vs $1000/T$ 85.5% PEO: 9.5% LiI : 5 % Al_2O_3	122
Figure 6.8(b): Plot of $\log \sigma$ vs $1000/T$ 81.0% PEO: 9 % LiI: 10 % Al_2O_3	123
Figure 6.8(c): Plot of $\log \sigma$ vs $1000/T$ 76 .5 %PEO : 8.5 % LiI : 15% Al_2O_3	123
Figure 6.8(d): Plot of $\log \sigma$ vs $1000/T$ 72.0%PEO:8%LiI:20% Al_2O_3	124
Figure 6.8(e): Plot of $\log \sigma$ vs $1000/T$ PEO-LiI- Al_2O_3 , 67.5% PEO : 7.5% LiI : 25% Al_2O_3	124
Figure 6.9(a): 87.3% PEO: 9.7% LiI :3% Calix4 at room temperature	127
Figure 6.9 (b) : 87.3% PEO : 9.7% LiI :3% Calix 4 at 70°C	128
Figure 6.9 (c) : 87.3% PEO : 9.7% LiI :3% Calix 4 at 100 ⁰ C.	128
Figure 6.10(a) : 87.3% PEO : 9.7% LiI :3% Calix6 at room temperature	129
Figure 6.10(b): 87.3% PEO : 9.7% LiI :3% Calix 6 at 70 ⁰ C.	130
Figure 6.10 (c): 87.3% PEO : 9.7% LiI :3% Calix 6 at 100 ⁰ C	131
Figure 6.11 (a): 89.1% PEO : 9.9% LiI : 1% Calix 4	132
Figure 6.11 (b): 88.2% PEO : 9.8% LiI : 2% Calix4	132
Figure 6.11(c): 87.3% PEO : 9.7% LiI :3% Calix4	133
Figure 6.11 (d): 86.4% PEO : 9.6% LiI : 4% Calix4	133
Figure 6.11(e): 85.5% PEO : 9.5% LiI : 5% Calix4	134
Figure 6.11(a): 89.1% PEO : 9.9% LiI : 1% Calix 6	134

Figure 6.11(b): 88.2% PEO:9.8% LiI:2% Calix6	135
Figure 6.11 (c): 87.3% PEO : 9.7% LiI :3% Calix6	135
Figure 6.11(d): 86.4% PEO:9.6% LiI:4% calix6	136
Figure 6.11(e): 85.5% PEO : 9.5% LiI : 5% Calix6	136
Figure 6.11: variation in ionic conductivity in PEO	137
Fig 7.1: Variation of (a) ϵ_r and (b) ϵ_i with frequency for PEO-LiI samples at 298 K	142
Fig 7.2: Variation of ϵ_r with frequency for various amounts of LiI in PEO based polymer electrolytes at 298K	143
Figure 7.3: Variation of (a) ϵ_r and (b) ϵ_i with $\log \omega$ for PEO:LiI (90wt. %:10wt. %) sample at different temperature.	144
Figure 7.4: Variation of ϵ_r and (b) ϵ_i with $\log \omega$ with various Frequencies for 90 wt. % PEO- 10wt. % LiI sample at different temperature	146
Figure 7.5: Variation of $\tan \delta$ with frequency for 90 wt. % PEO- 10 wt. % LiI polymer electrolyte at 298 K	147
Figure 7.6 : Variation of $\tan \delta$ with frequency for PEO-LiI sample at different temperatures.	148
Figure 7.7: Variation of (a) real (M_r) and (b) imaginary (M_i) parts of dielectric modulus as a function of $\log \omega$ for PEO-LiI sample at different temperature	150
Figure 7.8: Variation of (a) ϵ_r and (b) ϵ_i with $\log \omega$ of PEO-LiI- Al_2O_3 at different wt. % of Al_2O_3	152

Figure 7.9 : Variation of ϵ_r and (b) ϵ_i with $\log \omega$ for 15 wt.% of Al_2O_3 sample at different temperatures	153
Figure 7.10: Variation of (a) ϵ_i and (b) ϵ_r with $\log \omega$ For various frequencies for Al_2O_3 sample at different temperatures.	155
Figure 7.11: Variation of $\tan \delta$ with frequency for PEO-LiI- Al_2O_3 polymer electrolytes at 298 K.	156
Figure 7.12: Variation of $\tan \delta$ with frequency for PEO-LiI- Al_2O_3 sample at different temperature.	156
Figure 7.13: Variation of (a) real (M_r) and (b) imaginary (M_i) parts of the dielectric modulus as a function of $\log \omega$ for PEO-LiI- Al_2O_3 system at different temperatures.	157
Figure 7.14 : Variations of (a) ϵ_r and (b) ϵ_i with frequency for PEO-LiI-Calix4	159
Figure 7.15 : Variations of (a) ϵ_r and (b) ϵ_i with frequency for PEO-LiI-Calix6	160
Figure 7.16 : Variations of (a) ϵ_r and (b) ϵ_i with frequency for PEO-LiI-Calix4 [87.3% PEO : 9.7% LiI :3 wt.% Calix4] polymer electrolyte at different temperatures.	162
Figure 7.17 : Variations of (a) ϵ_r and (b) ϵ_i with frequency for PEO-LiI-Calix6 [87.3% PEO : 9.7% LiI :3 wt.% Calix6] polymer electrolyte at different temperatures	163
Figure 7.18 : Variations of (a) ϵ_r and (b) ϵ_i with $\log \omega$ for various frequencies of [87.3% PEO : 9.7% LiI :3 wt.% Calix4] polymer electrolyte at different temperatures.	164
Figure 7.19 : Variations of (a) ϵ_r and (b) ϵ_i with $\log \omega$ for various frequencies of [87.3% PEO : 9.7% LiI :3 wt.% Calix6] polymer electrolyte at different temperatures.	165

Figure 7.20 : Variations of $\tan\delta$ with frequency for various amounts of calix4 polymer electrolyte at 298 K	166
Figure 7.21 : Variations of $\tan\delta$ with frequency for PEO-LiI-calix4 [87.3% PEO : 9.7% LiI :3 wt.% Calix4] polymer electrolyte at different temperatures	166
Figure 7.22 : Variations of $\tan\delta$ with frequency for various amounts of calix6 polymer electrolyte at 298 K	167
Figure 7.23 : Variations of $\tan\delta$ with frequency for PEO-LiI-calix6 [87.3% PEO : 9.7% LiI :3 wt.% Calix6] polymer electrolyte at different temperatures	167
Figure 7.24: Variation of (a) real (M_r), and (b) imaginary (M_i) parts of the electric modulus as a function of $\log\omega$ for PEO-LiI-calix4 sample at different temperature.	168
Figure 7.25: Variation of (a) real (M_r), and (b) imaginary (M_i) parts of the electric modulus as a function of $\log \omega$ for PEO-LiI-calix6 sample at different temperature	169