Contents	Page No.
Acknowledgment	i-iii
Abstract	v-vi
Table of Contents	vii-xiv
List of Figures`	XV-XXV
List of Tables	xxvii-xxviii
List of Abbreviations	xxix
Chapter 1	3-38
1.1 Introduction	3
1.2 The Glass and It's Structure	4
1.2.1 Kinetics of Glass Formation	5
1.3 Fast Ionic Solids: Structure, Electrical Transport and	6
Applications	
1.3.1 Li ⁺ Ion Conduction in Glasses	8
1.3.2 Alternative Approaches to Enhance Ionic Conductivity	8
1.4 Ionic Conduction in Glasses	10
1.4.1 Anderson Stuart Model	12
1.4.2 Cluster Bypass Model	13
1.4.3 Diffusion Path Model	14
1.5 Review: Silica-gel Electrolytes and IL Confinement by Sol-gel	14
Process	
1.5.1 Stabilization of Silica-gels	17
1.5.2 Structure and Property Characterizations of Silica-gels	18
1.5.3 A Novel Class of Systems: Ionogels	20
1.5.4 Ionic liquids and Their Nano-confinements	22
1.5.5 Advance Applications of Confined IL Matrices	24
1.6 Supercapacitors	25
1.6.1 Applications of Supercapacitors	27
1.6.2 Status and Future Challenges	27
1.7 Gaps in Existing Research	27
1.8 Statement and Objective of the Work	29

Contents	Page No.
Chapter 2	39-78
Sample Preparation and Characterization Techniques	0, 10
2.1 Melt Quench Process	41
2.2 Sol-Gel Process	42
2.2.1 Hydrolysis and Polymerization	44
2.2.1a Reaction Mechanism of Hydrolytic Sol-gel Route	45
2.2.1b Reaction Mechanism of Non-Hydrolytic Sol-gel	46
Route	
2.2.2 Condensation	48
2.2.3 Drying and Dehydration	48
2.3 Characterization and Analytical Techniques	50
2.3.1 X-Ray Diffraction	50
2.3.2 Electron Paramagnetic Resonance Spectroscopy	53
2.3.3 Fourier Transform Infrared Spectroscopy	59
2.3.4 Field Emission Scanning Microscopy	60
2.3.5 X-Ray Photoelectron Microscopy	61
2.4 Thermal Studies	62
2.4.1 Differential Scanning Calorimetry	62
2.4.2 Differential Thermal Analysis	63
2.4.3 Thermogravimetric Analysis	64
2.5 Electrical Characterization	65
2.5.1 Electrical Conductivity	65
2.5.2 Impedance Spectroscopy	66
2.5.3 DC Polarization and Ionic Mobility	69
2.5.3.1 Galvanic Cell Method	70
2.5.3.2 AC/DC Method	71
2.5.3.3 Cyclic Voltammetry	72
2.6 Other Compositional Studies	73
2.6.1 Gravimetric Estimation	73
2.6.2 Density Measurements and Molar Volume Estimations	74

Contents	Page No
2.7 Software Used	74
Chapter 3	79-93
Structure and Properties of Lithium Doped Lead Cadmium	
Oxyhalide Glasses Prepared via. Melt Quench Process.	
3.1 Introduction	8
3.2 Composition Accuracy	8
3.3 Structural Characterization	8
3.3.1 Density and Molar Volume	8
3.3.2 Powder X-ray Diffraction	8
3.3.3 Powder X-ray Diffraction of Annealed Samples	8
3.3.4 Electron Spin Resonance Spectroscopy	8
3.3.5 FTIR Spectroscopy	8
3.4 Thermal Studies	9
3.4.1 Thermogravimetric Analysis	9
3.4.2 Differential Scanning Calorimetry	9
3.5 Temperature Dependence of Conductivity Cycles	9
3.6 Conclusions	9.
Chapter 4	99-23
Structure and Property Correlations of Ionic Liquid Confined	
Lithium Silica Gel Composites Prepared via. Sol-Gel Process.	
4.1 Introduction	10
System 4A	105-13
[EMIM] BF4 Confined Lithium Silicate Gel Composites Prepared by	
Hydrolytic Sol-Gel Process	
4A.1 Composition	10
4A.2 Structural Studies	10
4A.2.1 Density and Molar Volume	10
4A.2.2 Powder X-ray Diffraction	10
4A.2.3 Electron Paramagnetic Resonance Spectroscopy	110

Contents	Page No.
4A.2.4 FTIR Spectroscopy	113
4A.2.5 Field Scanning Electron Microscopy	115
4A.3 Thermal Analysis	118
4A.3.1 Differential Thermal Analysis	118
4A.3.2 Thermogravimetric Analysis	121
4A.4 Electrical Transport	122
4A.4.1 Impedance Spectroscopy	122
4A.4.2 Temperature Dependence of Conductivity	125
4A.4.3 DC polarization and Ionic Mobility	131
4A.4.4 Mechanism of Electrical Transport	133
4A.5 Conclusions	135
System 4B	137-151
[EMIM] BF ₄ Confined Lithium-Potassium Silicate Gel Composites	
Prepared by Hydrolytic Sol-Gel Process	
4B.1 Composition	139
4B.2 Structural Studies	139
4B.2.1 Density and Molar Volume	139
4B.2.2 Powder X-ray Diffraction	140
4B.2.3 Fourier Transform Infrared Spectroscopy	140
4B.2.4 Field Emission Scanning Electron Microscopy	141
4B.3 Thermal Analysis	142
4B.3.1 Differential Thermal Analysis	142
4B.3.2 Thermogravimetric Analysis	143
4B.4 Electrical Conductivity	144
4B.4.1 Impedance Spectroscopy	144
4B.4.2 Conductivity Cycles	146
4B.4.3 Ion Transfer Mechanism	150
4B.5 Conclusions	151
System 4C	153-173

[EMIM] BF4 Confined Lithium Silicate Gel Composites Prepared by Non-Hydrolytic Sol-Gel Process

Contents	Page No.
4C.1 Compositions	155
4C.2 Structural Studies	156
4C.2.1 Density and Molar Volume	156
4C.2.2 Powder X-ray Diffraction	157
4C.2.3 Electron Paramagnetic Resonance Spectroscopy	158
4C.2.4 FTIR Spectroscopy	159
4C.2.5 Field Emission Scanning Electron Microscopy	161
4C.3 Thermal Analysis	162
4C.3.1 Differential Thermal Analysis	162
4C.3.2 Thermogravimetric analysis	163
4C.4 Electrical Transport	163
4C.4.1 Impedance Spectroscopy	163
4C.4.2 Conductivity Cycles	168
4C.4.3 Mechanism of Electrical Transport	172
4C.5 Conclusions	174
ystem 4D	175-201

[BWHW] BI Commed Lithum Sincate Ger Composites Frepared by										
Hydrolytic	Sol-Gel	Route	and	the	Effect	of	Heavy	Metal	Ion	
Substitution	1.									

4D.1 Composition	177
4D.2 Structural Studies	178
4D.2.1 Molar Volume	178
4D.2.2 Powder X-ray Diffraction	179
4D.2.3 Electron Paramagnetic Resonance Spectroscopy	179
4D.2.4 FTIR Spectroscopy	180
4D.2.5 Field Emission Scanning Electron Microscopy	182
4D.3 Thermal Analysis	185
4D.3.1 Differential Thermal Analysis	185
4D.3.2 Thermogravimetric analysis	186
4D.4 Electrical Transport	186

Contents	Page No.
4D.4.1 Impedance Spectroscopy	186
4D.4.2 Conductivity Cycles	188
4D.3.3 Ion Transport mechanism	190
4D.5 Effect of Heavy Metal (Pb ⁺²) Ion Substitution	192
4D.5.1 Structural Studies	193
4D.5.1.1 Powder X-ray Diffraction	193
4D.5.1.2 Differential Thermal Analysis	193
4D.5.1.3 Thermogravimetric Analysis	194
4D.5.1.4 Field Emission Scanning Electron Microscopy	195
4D.5.2 Electrical Conductivity	196
4D.5.3 Ion Transport Mechanism	199
4D.6 Conclusions	200
System 4E	203-220
[EMIM] CF3SO4 Confined Lithium Silicate Gel Composites	
Prepared by Hydrolytic Sol-Gel Route	
4E.1 Compositions	205
4E.2 Structural Studies	206
4E.2.1 Density and Molar Volume	206
4E.2.2 Powder X-ray Diffraction	206
4E.2.3 FTIR Spectroscopy	207
4C.2.4 Field Emission Scanning Electron Microscopy	209
4E.3 Thermal Analysis	210
4E.3.1 Differential Thermal Analysis	210
4E.3.2 Thermogravimetric analysis	211
4E.4 Electrical Transport	211
4E.4.1 Impedance Spectroscopy	211
4E.4.2 Conductivity Cycles	215
4E.4.3 Conductivity Formalism	218
4E.5 Conclusions	219

Contents	Page No.
4F - Evidence for the Presence of IL in Solid Matrices	221-225
4F.1 Differential Scanning Calorimetry	223
4F.2 Electrical Conductivity Measurements	224
4F.3 X-Ray Photoelectron Spectroscopy	225
Chapter 5	235-267
Supercapacitor: A Potential Application of Silica Gel Solid	
Electrolytes for Energy Storage Devices	
5.1 Introduction	237
5.1.1 Supercapacitor Type	237
5.2 Experimental Procedures	238
5.2.1 Preparation of Electrode Material and Fabrication of	238
Supercapacitor	
5.2.2 Two Electrode Cell Configuration	239
5.2.3 Calculation for Capacitance Values	240
5.3 Exploring Application of IL Confined Silica-gels as	240
Supercapacitors: Preliminary Findings	
5.3.1 [EMIM] BF ₄ Containing Silica-gel Composites	243
5.3.1.1 Silica gel Composites having Only Lithium-ions	243
and No Potassium-ions. (Hydrolytic Process)	
5.3.1.2 Silica-gel Composites having Both Lithium and	248
Potassium-ions (Hydrolytic Process)	
5.3.1.3 Capacitance for Li ⁺ ion Containing Silica gel	251
Composites (Non-hydrolytic Process).	
5.3.2 [BMIM] Br Containing Silica-gel Composites	254
5.3.3 [EMIM] CF ₃ SO ₃ Containing Composites	258
5.4 Anamolous Behavior of Nyquist Plots	262
5.5 Conclusion	263
Chapter 6	269-277
Thesis Inferences and Future Scope of The Work	
6.1 Inferences	271

Contents	Page No.
6.2 Future Scope	276
Appendix A	279-291
(A1) List of Publications	281
(A2) Oral/Poster Presentations in National/International Conferences	283
(A3) Workshops Attended	285
Appendix B	
(B1) Brief Biography of Supervisor (Prof. S. C. Sivasubramanian)	287
(B2) Brief Biography of Supervisor (Prof. Anshuman Dalvi)	289
(B3) Brief Biography of Student (Mrs. Rajinder Kaswan)	291

Figure No.	Description	Page No.
Chapter 1		
1.1	Zachariasen's two-dimensional model of glass	4
1.2	Kinetics of glass transition	5
1.3	Typical DSC properties of (a) glass and (b) amorphous system	6
1.4	Paddle wheel mechanism for Li ⁺ ion transport in LiSO ₄	7
1.5	A pictorial view of two different configurational energies in the ionic transport in glasses	12
1.6	Schematic representation of cluster tissue concept for ionic transport	13
1.7	Potential energy diagram for conduction process in FIC glasses	14
1.8	The sol-gel process formation of silica gel composites	16
1.9	Major steps involved in preparation of silica gel composites	16
1.10	Schematic representation of hydration-dehydration process in stabilization of silica monoliths at different temperatures	17-18
1.11	σ -T for the pristine IL ([BMIM] TFSI) and a silica based ionogels	21
1.12	Physical confinement versus covalent grafting of IL on solid matrix	23
1.13	Energy and power density comparison of a battery and a supercapacitor.	26
Chapter 2	~	
2.1	Schematic diagram for sample preparation by melt-quench method	41

List of Figures

2.1	Schematic diagram for sample preparation by melt-quench	41
	method	
2.2	Schematic diagram for hydrolytic sol-gel process	46
2.3	Schematic diagram for non-hydrolytic sol-gel process	47
2.4	X-ray diffractometer (block diagram) and x-ray tube	51
2.5	EPR spectrometer, JEOL Japan (JES - FA200)	54
2.6	Schematic diagram for sample analysis in FTIR spectrometer	59
	in (a) ATR mode and (b) Transmission mode	
2.7	Schematic diagram of scanning electron microscope	61
2.8	Schematic diagram of XPS	61
2.9a	Schematic diagram of DSC instrument	62
2.9b	DSC scan for glassy samples	62
2.10	DTA 50 plus series SCHIMADZU setup	64
2.11	Schematic diagram of TGA instrument	65

Figure No.	Description	Page No.
2.12	Schematic diagram of sample holder used for electrical conductivity measurements (300-1000 K)	66
2.13	Schematic diagram for DC polarization setup, power supply and ammeter interfaced with PC	70
2.14	Plot of transient current <i>versus</i> time for ionic sample on applying a dc voltage	70
2.15	Experimental setup for Cyclic voltammetry	72
Chapter 3		
3.1	PXRD scan of LPCC series	86
3.2	PXRD scan of LPCC series annealed at 400 and 500 °C	87
3.3	EPR spectrum of LPCC series	88
3.4	FTIR spectrum of the composites	89
3.5	TGA scans for composites of LPCC series	90
3.6	DSC scans of the 30LPCC sample with different scan rates	91
3.7	T_g and T_p - T_g for samples of LPCC series	91
3.8	σ-T cycle for composites of LPCC series	92
3.9	The activation energy for ion transport versus composition	93
Chapter 4 System 4A		
[EMIM] BF	4 Confined Lithium Silicate Gel Composites Prepared by	
Hydrolytic S	ol-Gel Route	
4A.1	The photographic image at 1x magnification for densified gel obtained after room temperature drying the sol (before heating the composites).	108
4A.2	Molar volume of the composites of series-1(a) and series-2(b)	109
4A.3	PXRD patterns of the prepared samples (a) series-1 and (b) series-2	110
4A.4	PXRD pattern of the prepared samples (a) series-3 and (b) series-4	110
4A.5	EPR: RT-X-band spectrum for (a) increasing LiNO ₃ concentration, and (b) increasing IL concentration. Magnetic Field (H) values are in mT.	111
4A.6	EPR: RT (a) X-band and (b) the corresponding Q-band spectrum for L18 and L18E composites.	112
4A.7	L18 FTIR in (a) ATR mode and (b) in Transmission mode	113
4A.8	FTIR of the composites in (a) ATR mode (left) and (b) in transmission mode (right)	114

Figure No.	Description	Page No.
4A.9	Transmission mode FTIR spectra after heat treatment at 500	115
4 4 10	$^{\circ}$ C for L18 and L18E EESEM images of (a) L18 (b) L18E (c) L18E4 and (d) L26E	116
4A.10	FESEM images of (a) L18, (b) L18E, (c) L18E4 and (d) L26E samples	116
4A.11	EDS mapping over FESEM image for L18E composite	116
4A.12	EDS mapping of L18E Composite for various elements (a-f	117
	Left to Right- Si, O, F, N, C, and B)	
4A.13	EDS mapping over FESEM image for L18E composite after conductivity	117
4A.14	EDS mapping of L18E Composite after conductivity (a-d	117
	Left to Right-F, N, C, and B)	
4A.15	FE-SEM images of (a) L18, (b) L18E at 300nm and 200nm scale, respectively.	118
4A.16	SEM pictures of a sample (L26E) at different temperatures.	118
4A.17	DTA scan of the prepared composites (a) increasing $LiNO_3$	119
	concentration (Series-1) and (b) increasing IL concentration	
	(Series-2). Inset: An exothermic peak corresponding to the	
	boiling point of IL is evident (Clearly for higher IL containing (L18E7) composites).	
4A.18	DTA Plots of L33E normal run and repetition after cooling	120
111.10	without much time gap. Inset: DTA plot of L33E sample after	120
	three consecutive cycles of conductivity measurements and	
	after ~1 year (inset on a similar scale).	
4A.19	TGA scan of the prepared composites (a) increasing LiNO ₃	121
	concentration (Series-1) and (b) increasing IL concentration	
	(Series-2). Inset: TGA profile for neat IL.	
4A.20	Nyquist plots for best-conducting samples (a) L18 and (b)	123
	L18E. Inset in both shows time dependence of the dc-current.	
	For comparison, dimensions of the samples were kept almost	
4A.21	the same. Nyquist plots for best conducting samples with increasing	123
HA.2 1	salt content. Inset of both figures shows the time dependence	123
	of dc-current.	
4A.22	Electrical conductivity (σ) as a function of frequency (ω)	124
	from 200 – 300 °C (a) L18, (b) L18E, (c) L26E and (d) L33E.	
4A.23	$\sigma_{dc} \!-\! T$ cycle for composites with increasing $LiNO_3$	125
	concentration (Series 1).	
4A.24	σ_{dc} -T cycle for composites with increasing IL concentration	126
	(Series 2).	

Figure No.	Description	Page No.
4A.25	Variations of conductivity and activation energy with	127
	composition for series 1.	
4A.26	$\sigma_{dc}\text{-}T$ cycle for Series-3 composites. IL variation leads to a	127
	significant fall in conductivity	
4A.27	σ_{dc} –T cycle for Series 4 composites.	128
4A.28	L33E sample repetitive conductivity cycles in both heating	129
	and cooling pathways (30 °C to 300 °C).	
4A.29	σ–T cycle for (left) L18 and (right) L18E composites	130
	without copper L18-Cu and L18E-Cu.	
4A.30	Temperature dependence of electronic conductivity and total	131
	conductivity for L33E composite. Total conductivity is the	
	dc conductivity (also reported in Fig. 4A.23) as measured	
	using impedance spectroscopy.	
4A.31	Switching of the transient current of L33E sample and Ionic	132
	mobility (with 10 % error) of prepared samples (inset)	
4A.32	Scaling behavior of conductivity for Series 1 at 250 °C.	134
4A.33	Scaling behavior of conductivity for L33E with	134
	temperature.	
System 1P		

System 4B

[EMIM] BF₄ Confined Lithium-Potassium Silicate Gel Composites Prepared by Hydrolytic Sol-Gel Route

4B.1	XRD pattern of the prepared composites with KNO3	140
	substitution in a lithium silicate matrix.	
4B.2	FTIR in transmission mode (a) Series K1, (b) Series K2 and	141
	(c) Series K3.	
4B.3	FESEM images of L9K9 and L9K9E composites.	141
4B.4	FESEM images of L0K18 and L0K18E composites.	142
4B.5	Elemental mapping images of K18 and K18E composites.	142
4B.6	DTA scan of samples (Series-1).	143
4B.7	TGA of the prepared gel composites (Series-1).	143
4B.8	Nyquist Plots for (a) L9K9, (b) L9K9E, (c) L16K16E, and	144
	(d) L9K17E composites with temperature variations.	
4B.9	DC polarization for K9 and K9E composites.	145
4B.10	Frequency dependence of conductivity plots of (a) L9K9, (b)	145
	L9K9E, and (c) L16K16E composites with temperature	
	variations.	

Figure No.	Description	Page No.
4B.11	σ-T cycle of L9K9 and L9K9E composites.	146
4B.12	σ-T cycle of (a) Series-K1 and (b) Series-K2 composites.	147
4B.13	σ-T cycle of series-K3 composites	147
4 B .14	Scaling behavior of conductivity for (a) L9K9 and (b) L9K9E	150
	with temperature variation	
4B.15	Scaling behavior of L9K9 and L9K9E composites with salt	150
	content at 300 °C.	
g (10		
System 4C		
	Confined Lithium Silicate Gel Composites Prepared by Non-	
Hydrolytic S		1.5.5
4C.1	The photographic image at 1x magnification for stabilized	155
40.2	gel after drying homogeneous sol at room temperature.	150
4C.2	Molar volume plots for (a) Series 1, (b) Series 2 and (3)	156
40.2	Series 3.	157
4C.3	PXRD profile for the prepared samples via sol-gel non-	157
	hydrolytic route. (a) Series 1, (b) Series 2, and (c) Series 3.	150
4C.4	X-band EPR plots for the prepared samples via sol-gel non- budgelytic groute (a) Series 1. (b) Series 2. and (a) Series 2.	158
4C.5	hydrolytic route. (a) Series 1, (b) Series 2, and (c) Series 3.	158
40.5	Q-band EPR plots for the prepared samples via sol-gel non- hydrolytic route. (a) L18 and L18E, and (b) L33E and L46E	138
	composites.	
4C.6	FTIR for the composites prepared from the non-hydrolytic	159
40.0	sol-gel route in ATR mode (a) Series-1, (b) Series-2, and (c)	159
	Series-3.	
4C.7	FTIR for the composites prepared from the non-hydrolytic	160
40.7	sol-gel route in transmission mode (a) Series-1, (b) Series-2,	100
	and (c) Series-3.	
4C.8	FESEM images of non-hydrolytically prepared composites	161
	with increasing IL concentration (Series-2).	101
4C.9	FESEM images of non-hydrolytically prepared L33En and	161
	L46En composites (Series-1).	-
4C10	FESEM images of non-hydrolytically prepared composites	162
	from Series-3.	
4C.11	DTA scan for the composites prepared from the non-	162
	hydrolytic sol-gel route: (a) Series-1, (b) Series-2, and (c)	
	Series-3.	
4C.12	TGA scan for the composites prepared from the non-	163
	hydrolytic sol-gel route: (a) Series 1, (b) Series 2, and (c)	
	Series 3.	
4C.13	Nyquist Plots for L18n composite.	164

Figure No.	Description	Page No.
4C.14	Nyquist Plots for Series 1 composites.	166
4C.15	Nyquist Plots for (a) L33E3n, and (b) L40E3n composites	166
	from Series 3.	
4C.16	Electrical conductivity (σ') as a function of frequency (ω) for	167
	L18n and L18En composites in a temperature range of 250 –	
	350 °C.	
4C.17	Electrical conductivity (σ') as a function of frequency (ω) for	167
	(a) L40En, and (b) L46En composites with temperature	
	variations.	
4C.18	Electrical conductivity (σ') as a function of frequency (ω) for	168
	(a) L33E3, and (b) L40E3 composites with temperature	
	variations.	
4C.19	σ_{dc} -T cycle for (a) Series 1, and (b) Series 2.	168
4C.20	σ_{dc} -T cycle Series 3 composites.	170
4C.21	Scaling behavior of conductivity for (a) L18, (b) L26E, (c)	172
	L33E, and (d) L46E composites from series 1 with	
	temperature variations.	
4C.22	Scaling behavior of conductivity for (a) L33E3, (b) L40E3,	173
	and (c) L46E3 composites from series-3 with temperature	
	variations	1.50
4C.23	Scaling behavior of conductivity for (a) Series 1 and (b)	173
	Series 3 at ~300 °C.	
System 4D		
U	Confined Lithium Silicate Gel Composites Prepared by	
	ol-Gel Route and the Effect of Heavy Metal Ion Substitution.	
4D.1	Photographic images at 1x magnification for homogeneous	177
.2.11	sol kept at the ambient condition to for formation of a	177
	solidified gel.	
4D.2	Photographic images (magnification 1X of gel composites at	177
	1x magnification (from left to right the pictures correspond	
	to 10L, 10LB, 10L2B, 10L4B).	
4D.3	Molar volumes of the composites (a) series-1, (b) series-2	178
	and (c) series-3.	
4D.4	Powder X-ray Diffraction (PXRD) patterns of the as prepared	179
	composites of (a) series-1 and (b) series-2.	
4D.5	X-band (a) increasing IL concentration (b) Increasing LiCl	179
	concentration.	
4D.6	FTIR spectrum of the composites in the ATR mode (a)	181

4D.6 FTIR spectrum of the composites in the ATR mode (a) 181 series-1, (b)series-2 and (c) series-3.

Figure No.	Description	Page No.
4D.7	FTIR spectrum of the composites in normal transmission	181
	mode (a) series11, (b) series-2 and (c) series33. Samples were	
	in dry KBr matrix during the measurement.	
4D.8	FESEM images of (a) L10, (b) L10B, (c) L10B2 and (d)	182
	L10B4 samples	
4D.9	FESEM images of (left) L20B, (center) L25B, and (right)	183
	L30B samples	
4D.10	EDS mapping for L30B composite prior to conductivity-	183
	temperature cycles.	
4D11	EDS mapping for the fractured surface of L30B composite	184
	pellet. Measurements were done after a conductivity cycle	
	(30 – 300 °C).	
4D.12	ED Spectra of samples (a) L10 and (b) L10B.	184
4D.13	DTA scans of the as prepared gel composites (a) series 1 and	185
	(b) series 2.	
4D.14	TGA scan of the as prepared gel composites (a) series 1 and	186
	(b) series 2. Inset of Fig.: TGA for pure ionic liquid.	
4D.15	(a) Nyquist plots for L25B composite, and (b) Nyquist plots	187
	for L30B composite. Inset: Transient current obtained during	
	dc polarization measurement. Rapid fall in the current	
	followed by a saturation confirms ionic nature of these	
(D.1)	samples.	100
4D.16	log σ' as a function of frequency (ω) for (a) L20B, (b) L25B	188
4D 17	and (c) L30B with the increase in temperature.	100
4D.17	(a) Temperature dependence of dc conductivity for	188
	increasing LiCl content with fixed IL (1 mol%), and (b)	
	Temperature dependence of dc conductivity for samples with	
4D 19	increasing IL concentration and fixed salt content of 10 mol%	100
4D.18	Temperature dependence of dc conductivity for L25B and L 20B at ambient temperatures	190
4D.19	L30B at ambient temperatures. Scaling behavior of conductivity for L25B and L30B	191
4D.17	composites with temperature variation.	171
4D.20	The scaling behavior with composition variation. Scaling is	191
4D.20	missing in compositional variation.	171
4D.21	The photographic image at 1x magnification (a)	192
4D.21	Homogeneous sol of the composition (b) Prepared (solid) gel	192
	after annealing at 150 °C.	
	-	
4D.22	PXRD pattern of sol-gel synthesized amorphous composites.	193
4D.23	DTA of gel composites (a) increasing IL concentration and	194
	(b) increasing LiCl concentration.	

Figure No.	Description	Page No.
4D.24	TGA of gel composites (a) increasing IL concentration and	194
	(b) increasing LiCl concentration. TGA of Pristine BMIM Br	
	is shown in the inset.	
4D.25	FE-SEM image of (a) IL-free sample (L10P) and (b) L10PB	195
	at 500 nm scale.	
4D.26	EDS results for sample (a) L10P and (b) L10PB.	195
4D.27	Nyquist plots for gel sample (a) with no IL (L10P), and (b)	196
	with 1 mol% IL (L10PB)	
4D.28	Electrical conductivity (σ') has been plotted as a function of	197
	frequency (ω) for (a) L10P and (b) L10PB gel composites	
4D.29	(a) Electrical conductivity vs IL content at 300K. (a)	197
	Increasing IL for fixed LiCl concentration (10 mol%) (b)	
	increasing LiCl for fixed IL concentration (1 mol%).	
4D.30	Electrical conductivity versus temperature for different	198
	samples	
4D.31	Electrical conductivity versus temperature for different gel	199
	composites.	
4D.32	Scaling behavior of conductivity for L10P and L10PB with	200
	temperature.	
4D.33	Fig. 4D.33 Scaling behavior of conductivity for L10P and	200
	L10PB and S2 at ~50 °C.	
System 4E		
EMIM] CF	SO ₄ Confined Lithium Silicate Gel Composites Prepared by	
Hydrolytic S	ol-Gel Route	
4E.1	Photographic images at 1x magnification of the	205
	homogeneous densified gel (left) just before and (right) after	
	heating at 150 °C.	
4E.2	Molar Volume of the prepared composites (a) Series 1 and	206
	(b) Series 2.	
4E.3	XRD plots for (a) Series 1 and 3, and (b) Series 2.	207
4E.4	FTIR plots of the composites in ATR mode (a) Series-1 and-	207
	3, and (b) Series-2.	
4E.5	FTIR plots of the composites in transmission mode (a) mode	208

(a) Series-1 and -3, and (b) Series-2.
4E.6 Change in the structure of L18F, L18F13, L18F4, and L46F4 209 composites.
4E.7 EDS mapping of L18F and L18F13 composites. 210
4E.8 DTA plots for (a) Series-1, and (b) Series-2. 210
4E.9 TGA plots for (a) Series-1, and (b) Series-2. 211

Figure No.	Description	Page No.
4E.10	Nyquist plots for the composites with increasing IL and	212
	constant Li ⁺ ion content (18 mol%) – Series 2.	
4E.11	Nyquist plots for the composites of series-3.	213
4E.12	Nyquist plots for (a) L46F and (b) L46F4 composites in a	213
	temperature range of 250-350 °C.	
4E.13	Electrical conductivity (σ') as a function of frequency (ω)	214
	plots for the composites Series-2.	
4E.14	Electrical conductivity (σ') as a function of frequency (ω)	215
	plots for L33F4 and L46F4 composites.	
4E.15	σ-T plots for (left) Series-1 and (right) Series-2.	216
4E.16	σ-T plots for series-3 composites.	217
4E.17	σ-T plots for LiCF ₃ SO ₃ , L33F and L46F4 composites for	218
	comparision.	
4E.18	σ/σ_{dc} versus ω/ω_c plot for the composites of series-2.	218
4E.19	σ/σ_{dc} versus ω/ω_c plot for different compositions at ~300 °C.	219
4F.1	DSC plot of L18E composite	223
4F.2	Conductivities of L18 and L18E composites, before and after	224
	heat treatment at 500 °C for 24 hrs.	
4F.3	XP spectra of L18 and L18E7 composites.	225
Chanton 5		
Chapter 5 5.1	Preparation procedure for cathode material (a) Coconut	238
5.1		238
	shells, (b) Cathode preparation-cleaning process after cathode formation, (c) activated Charcoal (surface area 260	
	cannot formation, (c) activated Charcoar (surface area 200 m^2/g).	
5.2	Pellet obtained after applying the cathode paste.	239
5.3	Unit used for capacitance measurement.	239
5.4	(a) CV plots for series-1 from system 4B composites at room	237
5.4	temperature and (b) their corresponding impedance plots for	244
	comparison.	
5.5	CV plots for series-2 from system 4B composites at room	244
5.5	temperature and (b) their corresponding impedance plots for	277
	comparison.	
5.6	(a) CV plots for series-3 from system 4B composites at room	245
5.0	temperature and (b) their corresponding impedance plots for	215
	comparison.	
5.7	(a) CV plots for series-4 from system 4B composites at room	246
5.7	temperature and (b) their corresponding impedance plots for	2.0
	comparison.	
	I	

Figure No.	Description	Page No.
5.8	(a) Capacitance of L33E composite with change in Scan rate.	246
	Inset: A systematic increase in capacitance with Scan rate is	
	evident.	
	(b) Consequtive 12 CV cycles of L33E composite. Inset:	
	Capacitance variation is negligible up to 12 cycles.	
5.9	Comparison of Capcitance change with that of conductivity	247
	(RT) with Li salt concentration variation for the composites	
5 10	of series-1	2 40
5.10	(a) CV plots for only K^+ ion containing composites (series-	248
	4- system 4c) at room temperature and (b) their	
5.11	corresponding impedance plots for comparison.(a) CV plots for 50% K⁺ion substitution in Lithium	249
5.11	containing silica gel composites (discussed in section 5.2.2.1	249
	for L18 and L18E) at room temperature and (b) their	
	corresponding impedance plots for comparison.	
	corresponding impedance prote for comparisoni	
5.12	(a) CV plots for series-2 from system 4C composites at room	250
	temperature and (b) their corresponding impedance plots for	
	comparison.	
5.13	(a) CV plots for series-3 from system 4C composites at room	250
	temperature and (b) their corresponding impedance plots for	
	comparison.	
5.14	(a) Capacitance of L9K17E composite with change in Scan	251
	rate. (b) Consequtive 12 CV cycles of L9K17E composite.	
5.15	(a) CV plots for series-1 (system 4C) composites at room	252
	temperature and (b) their corresponding impedance plots for	
516	comparison.	252
5.16	(a) CV plots for series-2 from system 4C composites at room	252
	temperature and (b) their corresponding impedance plots for comparison.	
5.17	(a) CV plots for series-3 from system 4C composites at room	253
5.17	temperature and (b) their corresponding impedance plots for	200
	comparison.	
5.18	Capacitance of L46En composite with change in Scan rate.	253
5.19	Consequtive 12 CV cycles of L46En composite.	254
5.20	Cyclic-voltammogram of capacitors with different	255
	composites as separators (a) series-1 (b) series- 2 and (c)	
	series-3	
5.21	Impedance plots for capacitors with different composites (a)	256
	series-1 (b) series- 2 and (c) series-3	

Figure No.	Description	Page No.
5.22	CV plots for L10B4 and L30B composites (left) at room	257
	temperature and their corresponding impedance plots (right)	
	for a comparison.	
5.23	(a) CV plots for series-1 (system 4E) composites at room	258
	temperature and (b) their corresponding impedance plots for comparison.	
55.24	(a) CV plots for series-2 (system 4E) composites at room	259
	temperature and (b) their corresponding impedance plots for	
	comparison.	
5.25	(a) CV plots for series-1 from system 4E composites at	259
	room temperature and (b) their corresponding impedance	
	plots for comparison.	
5.26	(a) Capacitance of L46F composite with change in Scan rate.	260
	(b) Consequtive 12 CV cycles of L46F composite.	
5.27	Capacitance of L46F composite with temperature variation.	261
5.28	Capacitance of L46F composite with temperature variation.	261
5.29	Impedance plots for (a) L33E, (b) L40E and (c) L33E7	263
	composites, corresponding equivalent circuits are also mentioned.	

Table No.	Description	Page No.
Chapter 1		
1.1	Ionic conductivity enhancement in Li ⁺ ion oxide glasses	9
1.2	Some major achievement in field of sol-gel process	15
1.3	Characteristic IR bands of Si-O-Si network on hydrolysis and condensation of TEOS	19
1.4	Structure and physical properties of ILs	25
Chapter 2		
2.1	Comparison of glass forming ability of metal oxides by sol- gel process	43
2.2	Chemicals used in this work	49
2.3	Impedance plots and their equivalent electrical circuits	69
Chapter 3		
3.1	Composition, density and molar volume of the prepared lead-oxyhalide glasses	84
3.2	Precipitated particulate size after annealing at different crystallization temperatures	87
3.3	Conductivity at different temperatures and activation energy of glass composites	94
Chapter 4		
4.1	Composition, density and molar volume of the samples	107
4.2	Table 4.2: For various series of samples (i) Electrical conductivity at two different temperatures and (ii) The open-circuit voltage (OCV) of the Li/LiCoO ₂ cells fabricated using samples as an electrolyte.	129
4.3	Composition, Density and Molar volume of KNO ₃ containing composites	139
4.4	Activation energy (E_a) and conductivity (at 250 °C) of the composites.	148
4.5	Comparison of conductivities of composites with potassium substitution	149
4.6	Compositions, density and molar volume of the silica gel composites of non-hydrolytic processing.	155
4.7	Conductivity and activation energy of the composites of three different series.	171
4.8	Compositions of the samples: Sample codes have been used as abbreviations for compositions in the text.	178

List of Tables

Table No.	Description	Page No.
4.9	Electrical properties of the composites	189
4.10	Composition, density and molar volume of composites with [EMIM] CF ₃ SO ₃	205
4.11	Conductivity at different temperatures and activation energy for the samples at high temperature.	217
Chapter 5		
5.1	Measured capacitance and other relevant information for the composites prepared in this work.	241
5.2	Capacitance variation at high temperatures for L46F composite:	261
Chapter 6		
6.1	Some of the composites containing [EMIM] BF ₄ (prepared through hydrolytic process) and their conducting properties	273

$T_{ m g}$	Glass transition temperature
T _c	Crystallization temperature
T _p	Peak crystallization temperature
T _m	Melting temperature
DSC	Differential scanning calorimetry
FICs	Fast ionic conductors
SICs	Superionic conductors
NASICON	Sodium Superionic Conductor
σ	Conductivity
Odc	dc conductivity
$\sigma_{\rm e}$	Electronic conductivity
MAE	Mixed alkali effect
EDLC	Electrochemical double layer capacitor
SCs	Supercapacitors
MQ	Melt quench
DCCA	Drying control chemical additive
XRD	X-ray Diffraction
PXRD	Powder X-ray diffraction
FWHM	Full width half maximum
RDF	Radial distribution function
PDF	Pair distribution function
EM radiation	Electromagnetic radiation
ATR	Attenuated total reflectance
DTA	Differential thermal analysis
TGA	Thermogravimetric analysis
Ea	Activation energy
CV	Cyclic voltammetry
IS	Impedance spectroscopy
CPE	Constant phase element
OCV	Open circuit voltage
EMF	Electromotive force
RT	Room temperature
LNT	Liquid nitrogen temperature
[EMIM]BF ₄	1-Ethyl-3-methylimidazolium tetrafloroborate
[EMIM]CF ₃ SO ₃	1-Ethyl-3-methylimidazolium trifloromethanesulphonate
[BMIM]Br	1-Butyl-3-methylimidazolium bromide
LE	Lithium nitrate, [EMIM]BF ₄
LF	Lithium nitrate, [EMIM]CF ₃ SO ₃
LB	Lithium chloride, [BMIM]Br
LPB	Lithium chloride, Lead nitrate, [BMIM]Br
IL	Ionic Liquid