

1.1 Introduction

Lithium batteries have contributed extraordinarily to meet the challenges for eco-friendly high electric energy storage devices and have been proved pivotal in present day high-tech world. These devices laid the foundation of a portable, fossil fuel-free society. The significant achievements in the field by three pioneers viz; *M. Stanley Whittingham, John B. Goodenough, and Akira Yoshino* have won the chemistry Nobel 2019. Their work for the development of battery had an impact in portable electronic revolution [1].

Since, 1970's oil crisis laid the foundation of lithium-ion batteries, when M. Stanley Whittingham's (1970) and others approached for an alternative source for fossil-free energy sources. They designed the first functional rechargeable lithium battery from lithium metal (anode) and lithium-titanium disulphide (cathode). This has a strong preference for releasing electrons, making it very suitable for use in batteries. However, it had the risk of exploding on repetitive recharging.

Goodenough improved the cathode and replaced the titanium disulphide with cobalt oxide (in cathode) which boosted the lithium battery's potential to four volts. This cathode material as a basis was further used by Akira Yoshino to develop first commercially viable lithium ion batteries in 1985. These batteries used lithium ions with a carbon material called petroleum coke as the anode, with improved safety of Li-ion batteries. Based on Yoshino's configuration first commercial lithium-ion batteries were released by Sony in 1991. In his interview after the announcement of chemistry Nobel 2019 Goodenough stated, "... ..*We need to get burning fossil fuels off the highways and freeways of the world and focus on global warming and the battery storage is essential for a renewable energy future. If you are going to have renewable energy ... you need a battery where you can store it... Well, we're working on how to develop a polymer which has an immobilised liquid in it, so that it conducts lithium or sodium as fast as in the liquid. That's what we're working on and the liquid is immobilised so it's like a solid-state material.....*"

Present work is focused on the Li⁺ ion containing composites viz; (i) silica gel composites and (ii) lead oxyhalide glasses. We have tried to explore the structure and

electrical properties of these systems with focus mainly on ionic transport and its correlation with structure. Emphasis has been given on developing mechanisms of ionic transport. Ionic liquid confined silica gels are novel composites on which a significant attention has been given in the present work. A probable application of such composites in high capacitor device fabrication has also been attempted and it has been realized that with a good engineering of electrodes and interfaces such composites are useful electrolytes for solid-state of supercapacitor applications. This chapter presents a literature survey on Li^+ ion glasses. ILs confined gels with a central theme on structure and electrical properties. Various models developed to explain ionic transport has been reviewed.

1.2 The Glass and It's Structure [2]

The first investigator of glass structure was **Tammann** (1903), whose investigations defined glass as an “undercooled liquid”. He also tried to understand growth and nucleation process of crystallization in glasses. **Goldschmidt** (1964), focused on the glass forming ability of different materials. However, his concepts only succeeded for SiO_2 and GeO_2 based glasses and failed for systems derived from pure ionic oxides [3]. **Zachariasen** (1932) proposed glass formation rules universally known as Zachariasen's rules which were derived from A_xO_y oxides [4]. These can be summarised as:

1. Oxygen atom should not be linked to not more than two atoms
2. Number of oxygen atoms surrounding A should be small
3. Oxygen polyhedral shares the corner, neither the edges nor the faces
4. At least three corners in a polyhedral must be shared

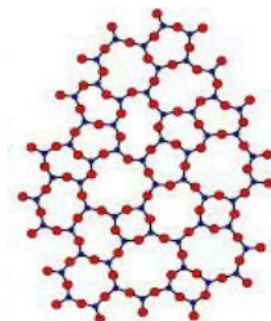


Fig.1.1 Zachariasen's two-dimensional model of glass [4].

As per Zachariasen's concept several oxides such as B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , As_2O_3 , Sb_2O_5 , Sb_2O_3 , In_2O_3 , Tl_2O_3 , SnO_2 , PbO_2 , P_2O_3 , As_2O_3 , Nb_2O_5 and Ta_2O_5 were categorised as 'natural glass formers' or 'network formers' while TeO_2 , SeO_2 , MoO_3 , WO_3 , BiO_3 , Al_2O_3 and V_2O_5 were categorized as 'intermediate network formers' or conditional glass formers. Oxides that disturb the bonding and the network framework were all 'network modifiers.' However, Zachariasen's model fails to explain glass-forming ability in non-oxide glasses [4].

Other structural models and theories that were also proposed for understanding the structure of glass, were Continuous Random Network (CRN) model (1966), Random Close Packing (RCP) model (1959, 1964), Smekel Theory (1951), Stanworth Theory (1946, 1952), Winter Theory (1955), Myuller concept (1960), Sun and Huggins concept (1947), Rawson concept (1956), and Sanderson's concept (1983).

1.2.1 Kinetics of Glass Formation

Formation of glass depends mainly on the quenching rate. For preparation of glass samples, the glass formation melt is heated above melting temperature (T_m). When the liquid is cooled below T_m and if the quenching rate is not very high, the crystallization takes place below T_m rapidly (Path 1). The process of crystallization occurs via nucleation and growth. But, if the glass forming melt is quenched rapidly (path 2), it leads to the formation of glass, also known as supercooled liquid, with glass transition (T_g) phenomenon (Fig. 1.2) [2].

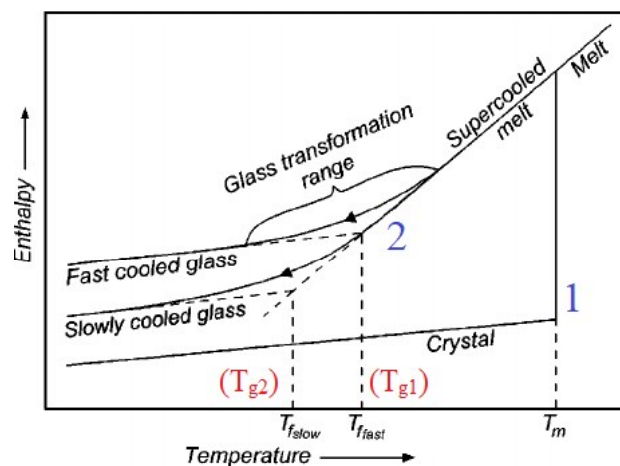


Fig. 1.2 Kinetics of glass formation [4].

Glasses exhibit striking thermal properties, which involves a complete understanding of phase transition and associated changes with variable temperature ranges. Thermal events of a material define any changes in its intensive properties particularly, structure. For glasses, primary events observed are glass transition (T_g), crystallization transition (T_c), and melting transition (T_m). Some of the other parameters that can be accounted with temperature changes are heat capacity (C_p), thermal expansivity (α) and volume compressibility (β) due to respective changes in Enthalpy (ΔH), Volume (V) and Entropy (S) [4].

The most important property of a glass that distinguishes them from other amorphous materials is the occurrence of T_g (Fig. 1.3). It marks for a temperature range up to which the glass is in its most relaxed state i.e. there are localized molecular relaxations (equilibrium) at T_g and it behaves as a frozen liquid below it. The process of glass formation is also known as vitrification, where the crystallization process is masked to achieve the amorphous state of the system. Structure of a glass is such that for $T \leq T_g$ frozen state, $T \geq T_g$ or $T_c > T > T_g$ local structural relaxations and structure is reproducible, and $T > T_c$ leads to permanent change in the structure.

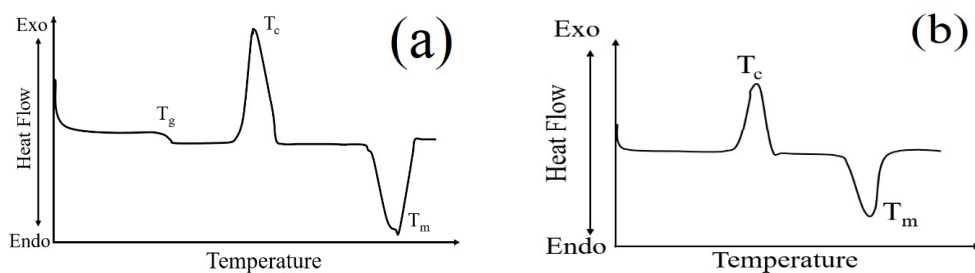


Fig. 1.3 Typical DSC profile of (a) glass, and (b) amorphous system.

Due to their liquid like structure glassy phase is an obvious choice for realization of a solid electrolytes.

1.3 Fast Ionic Solids: Structure, Electrical Transport and Applications

Liquid nature of an electrolyte in conventional electrochemical energy storage devices restricts their usages due to uneasy handling and poor durability. These limitations of an electrolyte conveniently and efficiently diverted the attention of material scientists towards the glass. Therefore, to enhance the conduction process, they are doped with

smaller conducting ions. Short-range order and liquid like structure marks the ion conduction process (hopping/jumping movements) along the ion gradient. Fast ionic/superionic conductors (FICs and SICs) have been discovered with an objective to replace the conventional liquid electrolytes.

Prior to ionic glasses, it is important to discuss fast ionic conduction in crystalline systems. Expedition of ionic conducting devices and the understanding for the motion of ions in FICs or solid electrolytes was initiated quite early [5-11]. Discovery of two important solid electrolytes, viz; Ag_2S and PbF_2 by Michael Faraday in 1833 laid the foundation of ionic conducting species [5, 6]. Later, in 1914 Tubandt *et al.* explored extraordinarily high ionic conductivity in solid AgI . It was revealed out that AgI exhibits two different phases viz; α -phase and β -phase. Above 147°C , β -phase of AgI transforms to α -phase which exhibit ionic conductivity of $\sim 1 \Omega^{-1}\text{cm}^{-1}$, whereas the β -phase of AgI exhibit ionic conductivity of $\sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$. α -phase of AgI was the first discovered superionic conductor [6]. This breakthrough lead to the discovery of other highly conducting ions Li^+ , Cu^+ , Na^+ etc. High ionic conductivity of Li^+ ion was initially determined in α phase of Li_2SO_4 , LiN_3 [7, 8]. With gradual understanding of the structure and conducting phenomenon in solid electrolytes, necessity of disordered structure for fast ion conduction was appreciated. The presence of open channels with moderate energy barriers in such systems was the major reason behind their high electrical conducting properties. This understanding lead to the discovery of ionic transport in glasses [9], mixed crystals [10], and polymers [11].

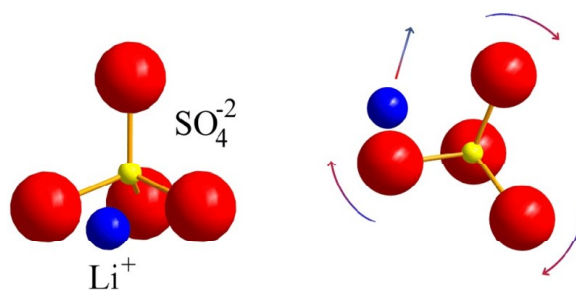


Fig. 1.4 Paddle wheel mechanism for Li^+ ion transport in Li_2SO_4 [7].

High ionic conduction was initially discovered in Li_2SO_4 crystalline solids [12], at $\sim 575^\circ\text{C}$, where a highly disordered phase (α - Li_2SO_4) of Li_2SO_4 enables superionic conductivity of $\sim 1 \Omega^{-1} \text{cm}^{-1}$ much below melting point. Structural investigations reveal

that α -Li₂SO₄ phase exhibits an isolated SO₄²⁻ tetrahedral in FCC lattice arrangement that undergoes rapid rotations around S⁶⁺ centre. Fast rotation of SO₄²⁻ facilitates Li⁺ ion diffusion through an interesting paddle wheel mechanism [7].

High Li⁺ ion conductivity near room temperature was also observed in Li₃N crystals [8, 13]. Layered structure of Li₃N forms N-Li-N bridges, through which the Li⁺ ion conducts and exhibits high ionic conductivity of $\sim 10^{-4} \Omega^{-1} \text{ cm}^{-1}$. But, low decomposition potential (0.445 V) of Li₃N restricts its usages in device applications [13]. Among lithium oxides, perovskite type compounds have also drawn interest e.g. Li_{2/3-3x}La_xTiO₃ (LLTO) showed high bulk ionic conductivity of $\sim 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at room temperature [14]. Similarly, the NASICON structured Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) showed high bulk ionic conductivity of $\sim 3 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at room temperature that is indeed comparable to aqueous solutions [15]. Both these compounds, however, exhibit poor grain boundary ionic transport.

1.3.1 Li⁺ Ion Conduction in Glasses

Li⁺ ion conducting electrolytes favours high voltages and high specific energy densities due to small size and electropositive nature of Li⁺ ion. Fast Li⁺ ion conduction in various glasses were initially investigated by Otto (1966) [16], and can be generally categorised either into oxide or sulphide glasses. As the present work focuses on lithium oxide systems, these will only be discussed briefly.

A network former oxide (SiO₂, B₂O₃, etc.) forms oxide glassy state whereas a network modifier (Li₂O) alters the glass structure. Literature findings report that lithium oxide glasses exhibit very low room temperature conductivity ($\sim 10^{-7} - 10^{-8} \Omega^{-1} \text{ cm}^{-1}$) [17, 18]. However, formation of non-bridging oxygen at the expense of bridging oxygen by substitution of metal oxide (Li₂O-M_xO_y systems) can lead to a rise in conductivity by few orders [19].

1.3.2 Alternative Approaches to Enhance Ionic Conductivity

Suitable compositional variations in Li₂O based glasses makes them promising/potential candidate for high temperature solid ionic devices. The ionic transport in lithium oxide systems can be increased by:

- (i) Addition of salt (for e.g. Li₂SO₄, LiCl), which increases the concentration of mobile charge carriers [19].

- (ii) Use of mixed glass formers (e.g. $P_2O_5 - B_2O_3$), can essentially increase the free volume of the glass matrix that eventually lead to fast ion conduction [20].
- (iii) It is possible to form Li^+ ion-based glass-ceramics by heat treatment of dense glass of suitable composition. This leads to precipitation of embedded fast ionic crystallites (for eg. Li^+ ions containing NASICON, $LiTi_2(PO_4)_3$ (LTP) etc.) [21].

Literature regarding the ionic conductivity enhancement in Li^+ ion oxide glasses has been listed in Table 1.1.

Table 1.1 Ionic conductivity enhancement in Li^+ ion oxide glasses.

S. No.	Composition	Conductivity ($\Omega^{-1}cm^{-1}$)	Reference No.
1	56Li ₂ O-8LiF-36B ₂ O ₃	6×10^{-4} (300 °C)	23
2	56Li ₂ O-8LiCl-36B ₂ O ₃	10^{-3} (300 °C)	23
3	56Li ₂ O-8LiBr-36B ₂ O ₃	1×10^{-3} (300 °C)	23
4	56Li ₂ O-8LiI-36B ₂ O ₃	3×10^{-3} (300 °C)	23
5	40Li ₂ O-55B ₂ O ₃ -5LiNbO ₃	2×10^{-4} (350 °C)	24
6	40Li ₂ O-6Y ₂ O ₃ -54SiO ₂	10^{-3} (300 °C)	25
7	50Li ₄ SiO ₄ -50Li ₃ BO ₃	4×10^{-6} (25 °C)	26, 27
8	50Li ₂ O-30P ₂ O ₅ -20As ₂ O ₃	3×10^{-3} (275 °C)	28
9	41.1 Li ₂ O-30P ₂ O ₅ -4.1As ₂ O ₃ -17.6LiCl	7×10^{-3} (275 °C)	28
10	35Li ₂ O-35P ₂ O ₅ -30MoO ₃	1×10^{-8} (25 °C)	29
11	Li ₂ O-TiO ₂ -P ₂ O ₅	$10^{-2} - 10^{-5}$ (127 °C)	30
12	20Li ₂ O-80Bi ₂ O ₃	7.1×10^{-9} (200 °C)	31
13	Li ₂ SO ₄ -Li ₂ O-P ₂ O ₅	$\sim 10^{-7}$	32
14	50.5Li ₂ O-0.5Al ₂ O ₃ -9TiO ₂ -40P ₂ O ₅	2×10^{-2} (350 °C)	33
15	50Li ₂ O-50(0.5SeO ₂ -0.5B ₂ O ₃)	8×10^{-7} (25 °C)	18
16	45Li ₂ O-50B ₂ O ₃ -5V ₂ O ₅	10^{-7} (25 °C)	34, 35
17	35Li ₂ O-35P ₂ O ₅ -30LiBO ₂	5×10^{-5} (152 °C)	36
18	47Li ₂ O-53(0.5B ₂ O ₃ -0.5P ₂ O ₅)	10^{-7} (25 °C)	37
19	50Li ₂ O-30P ₂ O ₅ -20B ₂ O ₃	2×10^{-5} (110 °C)	38

S. No.	Composition	Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Reference No.
20	50Li ₂ O-50P ₂ O ₅	5×10^{-4} (280 °C)	39
21	28Li ₂ O-60P ₂ O ₅ -12In ₂ O ₃	1×10^{-7} (120 °C)	40
22	35Li ₂ O-10PbO-30.25B ₃ O ₄ -24.75P ₂ O ₅	10×10^{-8} (25 °C)	41
23	50Li ₂ O-45P ₂ O ₅ -5Nb ₂ O ₅	10^{-4} (280 °C)	42
24	25Li ₂ O-50V ₂ O ₅ -25P ₂ O ₅	5×10^{-8} (25 °C)	43
25	66.7Li ₂ O-33.3P ₂ O ₅	-	44
26	Na ₂ O-Li ₂ O-P ₂ O ₅	-	45
27	50SiO ₂ -30B ₂ O ₃ -xLi ₂ O-(15-x)Y ₂ O ₃	10^{-6} (620 °C)	46
28	xLi ₂ O-(1-x)(0.75B ₂ O ₃ -0.25SiO ₂)	3.6×10^{-6} (25 °C)	47
29	33.5Li ₂ O-66.5P ₂ O ₅ -xV ₂ O ₅	$\sim 10^{-7} - 10^{-10}$ (25 °C)	48
30	60Li ₂ SO ₄ -40LiPO ₃	$\sim 10^{-4} - 10^{-5}$ (100 °C)	49
31	60Li ₂ SO ₄ -40(Li ₂ O-P ₂ O ₅)	$\sim 10^{-5} - 10^{-6}$	50

1.4 Ionic Conduction in Glasses

A glassy material exhibits liquid like structure due to which a lot of free space/volume is available for the charge carriers to move. Total conductivity (σ) of the glass is equal to the sum of the conductivities of all the charge carriers in the glass and is represented as $\sigma = \sum t_i \sigma_i$, where t_i is the transport number and σ_i is the conductivity of the i^{th} charge carrying species. Glasses exhibit single ionic species as a charge carrier ($t_i \approx 1$). So, for single ion conducting sample, conductivity can be [2] -

$$\sigma = \sigma_i = n|Z_e|\mu \quad (1)$$

Where, n is charge carrier concentration, Z_e is charge and μ is mobility of the i^{th} species of mobile charge carrier. On applying an external field (E) charges diffuse in the matrix and this force is $Z_e E$. Concentration gradient of the diffusing ion works in opposite direction, this force is $(kT/n) \cdot \nabla n$ where, n is concentration, ∇n is concentration gradient, T is temperature and k is Boltzmann constant. Dynamic fluxes arise by above phenomenon

$$D\nabla n = n v_d \quad (2)$$

Where D is diffusion coefficient and v_d is drift velocity. D can be represented as

$$D = kT(v_d/Z_e E) = [kT/(Z_e)]\mu \quad (3)$$

here, $\mu = (v_d/E)$. From Equation, 1 and 3 we have Nernst equation relation,

$$D = \sigma kT/n(Ze)^2 \quad (4)$$

Diffusion coefficient is also related to jump frequency (Γ) i.e. distance between two active sites (λ) as

$$D = 1/6 \lambda^2 \Gamma \quad (5)$$

from Equation 4 and 5,

$$\sigma = [(n(Ze)^2 \lambda^2)/6kT]\Gamma \quad (6)$$

Jump frequency is a thermally activated process and is related to cation vibrational frequency V_0 . From thermodynamic relation $\Delta G_m = \Delta H_m - T\Delta S_m$, Γ can be expressed as

$$\Gamma = v_0 \exp((\Delta S_m)/k)\exp(-(\Delta H_m)/kT) \quad (7)$$

Where, ΔS_m and ΔH_m are entropy and enthalpy terms. Applying Equation 7 into 6 we have,

$$\sigma = \sigma_0 \exp[-(\Delta H_m)/kT] \quad (8)$$

Where,

$$\sigma_0 = v_0 \exp(\Delta S_m/k) \quad (9)$$

In Equation 8, ΔH_m term can be related to $\Delta E_m (\approx E_a)$ expressed as,

$$\sigma = \sigma'_0/T \exp[-E_a/kT] \quad (10)$$

E_a can be determined through the plot between σ and $1/T$. Conductivity can be correlated with the activation energy in simple Arrhenius form as

$$\sigma = \sigma_0 \exp[-E_a/kT] \quad (11)$$

Motion of single ionic (either cation or anion) species determines the conduction process and the equation 11 makes it clear that the ionic conductivity of glasses should exhibit Arrhenius behaviour for $T < T_g$.

Various other theoretical models have also been proposed to understand the ion transport mechanism in glassy systems. The most widely applicable to the Li^+ ion motion in composites has been discussed.

1.4.1 Anderson Stuart (AS) Model

It defines the motion of ions to be a hopping mechanism must overcome comparable sites separated by a certain energy barrier [51]. In the process, ions work against two forces; (i) columbic interactions (force which holds up ions), (ii) doorway interactions (passage for the motion of ions). Mainly oxide glasses have both bridging oxygen (BO) and non-bridging oxygen (NBO) where this model is generally applicable. For the motion of ions, open doorways are required. Further, the compression in adjacent oxygen atoms pushes the ion in forward direction. This entire process needs some activation energy, which is sum of electrostatic binding energy and strain energy (Fig. 1.5).

$$E_a = E_b + E_s \quad (12)$$

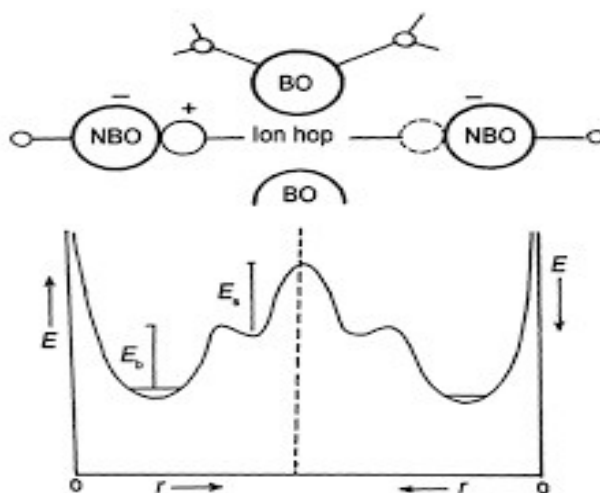


Fig. 1.5 A pictorial view of two different configurational energies in the ionic transport in glasses. [51, 52]

After incorporating all other factors of correction, E_a is given by,

$$E_a = (\beta ZZ_0 e^2)/(\gamma(r+r_0))+4\pi G r_D (r-r_D)^2 \quad (13)$$

Here, β is Madelung type constant, $\gamma = \epsilon$ i.e. relative dielectric permittivity. The concept fits for alkali silicate glasses but had limitations in terms of ϵ and λ .

The model was therefore given in relationships of inter carrier distances (proved unsuccessful). For example, for oxide glass of Na^+ ion the activation energy is given by

$$E_a = B_1 + B_2 [1/(r_o + r_{\text{Na}}) - 1/R] \quad (14)$$

1.4.2 Cluster Bypass Model

Cluster Tissue Concept of T_g was proposed by Ingram *et al.* to understand ionic conduction in glasses [53, 54]. As per the concept, the presence of highly disordered phase in form of micro domains or inter-cluster space of size $\sim 25\text{-}50 \text{ \AA}$ are embedded in the ionic glass. Below T_g , the residual liquid exhibits a residual phase which is also known as “connective tissue”. This tissue provides pathways to the charge carriers. Curvature in Arrhenius plot is due to continuous motion of ions between cluster and the tissue region.

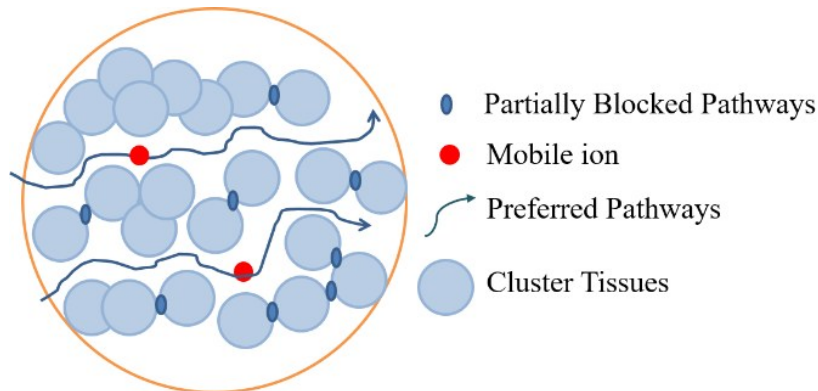


Fig. 1.6 A schematic representation of cluster tissue concept for ionic transport [55].

The model was also explored for mixed alkali systems [55], where it is suggested that the presence of foreign alkali cations in Li_2O ionic systems results into restricted pathways for the mobile charge carriers leading to high dielectric losses (Fig. 1.6). The model was also analysed for some AgI based glassy ionic systems and its validation was done with other experimental techniques like neutron diffraction [56], EXAFS [57, 58].

1.4.3 Diffusion Path Model

In 1985 Minami, proposed that the sites with comparable potential energy defines the conductivity path [59]. The FIC glasses were explored for diffusion path model mainly for Ag^+ and Li^+ ions. Initially the effect of addition of LiSO_4 and Li-halides was studied in Lithium borosilicate glasses with attainable conductivity of $10^{-4} \text{ S cm}^{-1}$ at 100°C . Availability of polarized ions increases decoupling index as well as conductivity. So, conductivity of 10^{-3} S m^{-1} , with decoupling index of 1012.5 at T_g was obtained for lithium thiophosphate glasses. Similarly, in other ionic systems like $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiI}$, $\text{Li}_2\text{O-B}_2\text{O}_3$ to $\text{Li}_2\text{S-B}_2\text{S}_3$ low conductivity $\sim 10^{-9} \text{ S m}^{-1}$ at room temperature was recorded. Henceforth, two important conclusions were drawn from the above compositions

- (i) Substitution of $\text{O} \rightarrow \text{S}$ increases room temperature conductivity. Because polarization energy contributes in reducing energy barrier by increasing anion polarizability.
- (ii) Dissolution of salts enhances conductivity in same manner as polarizability of anions i.e. $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.

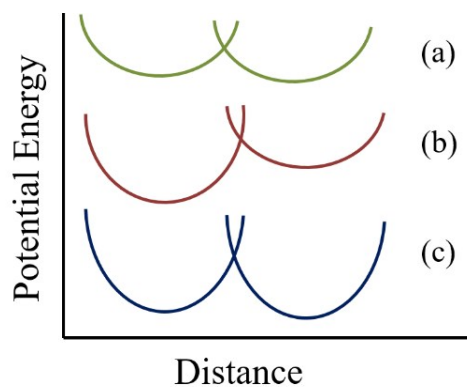


Fig. 1.7 Potential energy diagram for conduction process in FIC glasses. (a) shallow-shallow, (b) deep-shallow, and (c) deep-deep potential wells [59]

1.5 Review: Silica-gel Electrolytes and IL Confinement by Sol-gel Process. [60]

Sol-gel science is an ancient technique, which provides an alternative for preparation of ceramics and glassy materials at reasonably low temperature. It gives an advantage of preparing the composites in utmost homogeneity that are otherwise difficult to prepare through conventional processes. J. J. Ebelman (1980's) initially described the synthesis

of silica by slow hydrolysis of silicic ester in presence of moisture using sol-gel process. However, an active research in sol-gel science began in late 1990's. Beauty of this process is the chemically controlled mechanisms i.e. the choice of reaction parameters and the procedure followed plays an important role in tailoring the final product with desired properties.

Table 1.2: Some major achievements in the field of sol gel process [61]

Discoverer	Year	Contributions
Van Helmont	1640	Discovered 'water glass' on acidification of silica gel.
Ebelman	1845	Discovered the formation of transparent glass on atmospheric exposure of silane made from SiCl ₄ and ethanol.
Patrick	1913	Discovered the economic method of silica gel preparation in large quantities.
Kistler	1931	Discovered the process of formation of aerogels by supercritical drying.
Geffecken and Berger	1939	Sol-gel method was used for preparing single oxide coatings
Dickey	1949	Specific silica adsorbents
Nicolaon and Teichner	1968	Alkoxide route to aerogels
Stober	1968	Silica nano-sols
Avnir	1984	Doped sol gel materials
Schmidt	1985	Organically modified silicates (ORMOSILs)
Carturan	1989	Immobilization of micro-organisms in silica matrices.
Avnir	1990	Immobilization of enzymes in silica matrices
Boeing	1998	Sol gel coatings replaced chromates
Bright	1998	Low cost O ₂ optical sensor on Ru-doped luminescent material
Toshiba	1998	Sol-gel coating for TV screens
Bottcher	1999	Liquid embedding in nano-sols
Ozin	1999	Periodic mesoporous organosilicas
De Vos and Verweij	1999	Long lasting ORMOSIL –based membranes
Hench	2000	Third generation tissue regeneration materials – bio-glass by sol gel process.
Cabot Cop.	2003	Production of silica aerogels under ambient conditions
SiliCycle	2007	Commercialization of multi-component
Su	2008	Photosynthetic bioreactors – silica entrapped cyanobacteria
Warren and Wiesner	2012	Metal nanoparticles doped silica gels for extraordinary conductivity

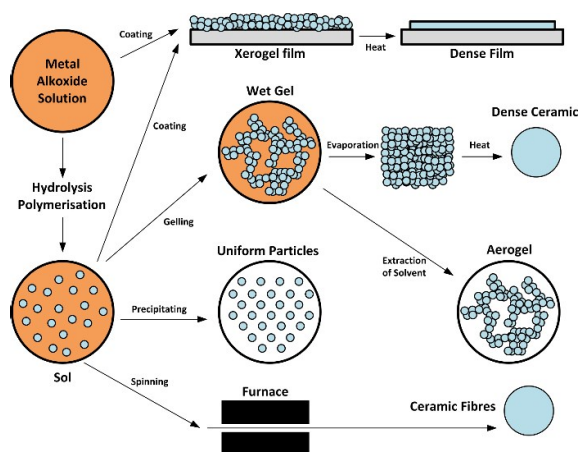


Fig. 1.8 The sol gel process and formation of different products [64].

The sol-gel process can be performed by two different procedures, (i) hydrolytic process and (ii) non-hydrolytic process. Both the processes differ in their hydrolysis step. In case of hydrolytic process, the process of hydrolysis begins in presence of acidic/basic catalyst. Another co-solvent (alcohol, methanol etc.) is generally employed for the promotion of hydrolysis procedure. Acid catalysed gels express high bulk density, clarity, surface area, fine and narrow pore size distribution as compared to the base catalysed gels. On the other hand, the non-hydrolytic process focuses on the use of carboxylic acids e.g. formic acid and trifluoroacetic acid, where the carboxylic acid plays the role of catalyst as well as the solvent. Literature findings report for faster rate of gel formation than corresponding aqueous procedures [62, 63]. Major steps involved in preparation of these silica gel composites for the doctoral work are: (i) Hydrolysis, (ii) Gelation/condensation, (iii) Aging and (iv) Drying (Details in chapter 2).

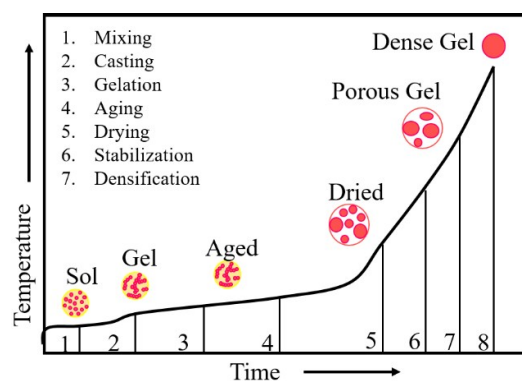


Fig. 1.9 Major steps involved in preparation of silica gel composites [64].

1.5.1 Stabilization of Silica-gels

Materials need to be stabilized chemically and thermally for the energy device applications. Literature findings reveals the presence of chemisorbed hydroxyls even on the surface of dried gels [64]. The chemical stabilization of these materials is in terms of removal of these hydroxyls and silanols below a critical level. One of the major drawbacks of the sol-gel procedure is the complete dehydration of the surface prior pore closure. On a silanol (Si-OH) surface the hydroxyl groups are present in two different forms, (i) chemisorbed (hydroxyl groups associated with the gel surface) and (ii) physisorbed (free water within the ultra-pores).

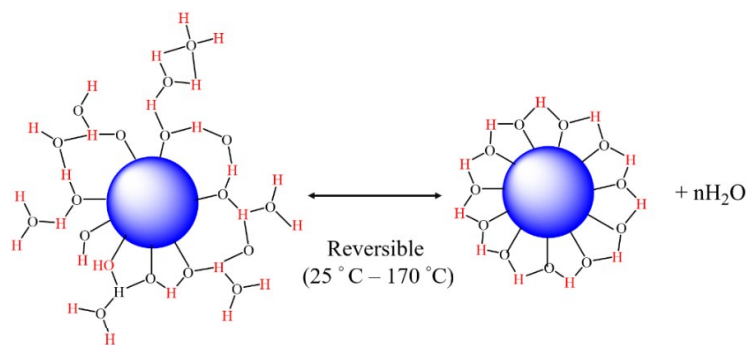


Fig. 1.10a Condensation of physical water and silanol groups (25 °C – 170 °C).

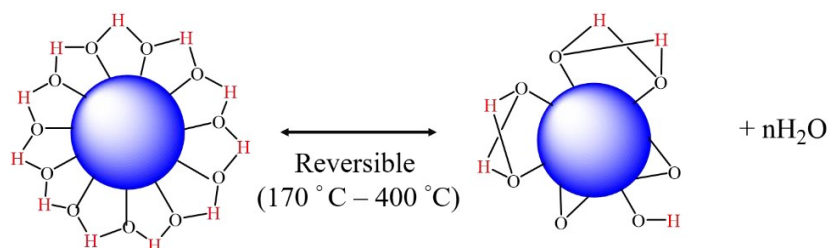


Fig. 1.10b Condensation of surface silanol groups are reversible in range of 170 °C – 400 °C.

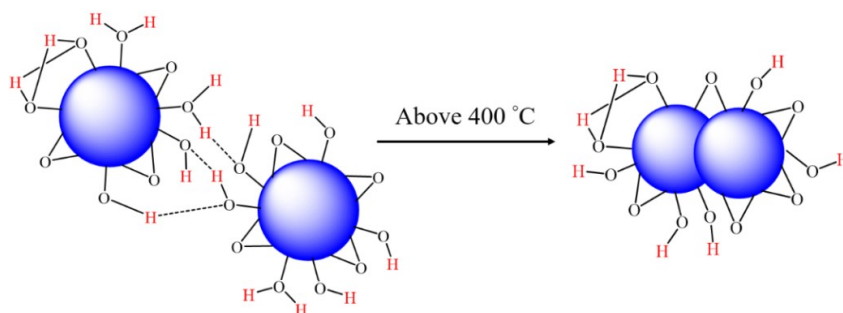


Fig. 1.10c Irreversible elimination of adjacent hydroxyl groups (above 400 °C).

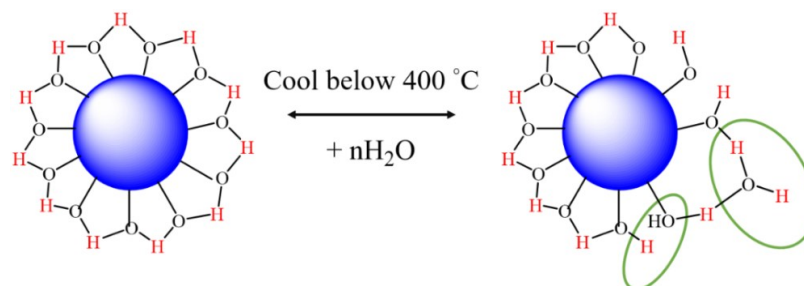


Fig. 1.10c Reabsorption of physical water below 400 °C.

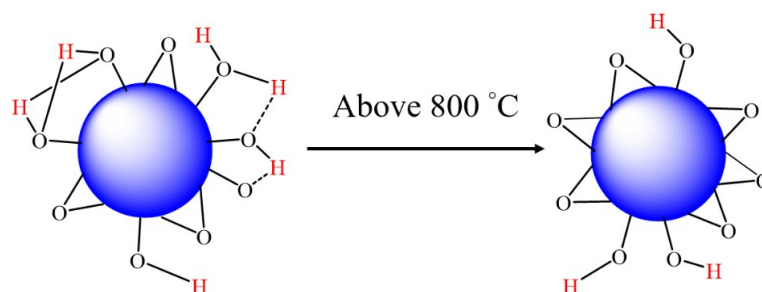


Fig. 1.10d Stable glass: remaining isolated hydroxyl groups (above 800 °C).

Fig. 1.10 (a-d) Schematic representation of hydration-dehydration process in stabilization of silica monoliths at different temperatures [64].

Literature finding explains thoroughly that the physisorbed water eliminates around $\sim 100\text{--}170$ °C along with some elimination of chemisorbed water. However, the dehydration process remains reversible up to 400 °C. This temperature range is also marked for the removal of other organic residues present in the matrices. The process of complete dehydration of chemisorbed hydroxyls occurs on heating the composites above 400 °C and a completely dehydrated material could be obtained after heating the composites above 850 °C. This leads to the formation of completely densified systems. This whole process of hydration and dehydration can be understood from Fig. 1.10.

1.5.2 Structure and Property Characterizations of Silica gels

The sol gel process is well known for its implication in preparation of advance materials since long. One such attempt was from Levy *et al.* in preparing optical fibre devices from ormosils and ormocers [65]. Yamane *et al.* attempted introduction of heavy metal ions (Pb^{2+}) in amorphous composites (PbO-SiO_2) for the fabrication of gradient index (GRIN) glass rods with variable refractive index. It was then analysed the difficulty for

homogeneous introduction of heavy metal ions, as ~24% of Pb was concentrated in the centre whereas ~20% of it was present at the perimeter [66].

Table 1.3: Characteristic IR bands of Si-O-Si network formation on hydrolysis and condensation of TEOS [67]

S. No.	IR Band (cm ⁻¹)	Description
1.	3500-3000	OH stretching (EtOH, H ₂ O, TEOS)
2.	1416-1324	O-H bending, C-H Wagging (CH ₂ in TEOS, EtOH)
3.	1200	Si-O-Si asymmetric stretching in cyclic structure
4.	1147	Si-O-Si asymmetric stretching in linear structure
5.	1100	Si-O-Si symmetric stretching in linear structure
		C-O asymmetric stretching TEOS
6.	1086	Si-O-Si symmetric stretching in cyclic structure
		C-O asymmetric stretching EtOH
7.	960	C-H rocking (CH ₃ in TEOS)
8.	920	Si-O non bridging (free/broken network)
9.	793	SiO ₄ asymmetric (TEOS)
		Si-O-Si bending (SiO ₂)
10.	475	-O-C-C deformation (TEOS)
		-O-Si-O- (bending SiO ₂)

Materials science pioneers have explored the formation of silica network from silicon oxide through sol-gel process and their structural features have been explored through a wide range of spectroscopic and non-spectroscopic investigations [64-74]. The process of tetraethoxysilane (TEOS) hydrolysis and formation of Si-O-Si units were investigated by Rubio *et al.* using FTIR spectroscopy [67]. The characteristic IR peaks for silica network at 1168 and 812 cm⁻¹ were used to understand the hydrolysis procedure whereas the process of polymerization was investigated through 1200 and 1147 cm⁻¹ peaks. The process of hydrolysis was observed to be low in absence of catalyst (acid or base). With the formation of silica network, the intensity of IR peaks corresponding to TEOS decreases slowly at 473, 1102 and 1168 cm⁻¹ and the intensity of 460, 1168 and 1200 cm⁻¹ peaks increases progressively with the formation of Si-O-Si network. At this stage, the system remains in form of a 'sol'. Polymerization of Si-OH groups to form three-dimensional Si-O-Si network was examined by 1200 and 1147 cm⁻¹ IR peaks. Increase in

intensity of $\sim 1200\text{ cm}^{-1}$ peak was marked for three-dimensional Si-OH crosslinking. Further, the peaks at 960, 920 and 763 cm^{-1} were also associated to un-polymerised Si-OH, Si-O⁻ and SiO₄ bonds of xerogels [67]. Table 1.3 summarizes some of the characteristic IR bands of silica network.

Literature findings state that the silica-based systems are the most explored among the sol-gel processed systems. These studies can be classified into three categories viz., where (i) only Li⁺ ions are added [68, 69], (ii) only pure ionic liquid is added [70-72], (iii) both Li⁺ ions and ionic liquids are added to the framework [73, 74].

In a study Rao et al. explored lithium silicophosphate glasses for Li⁺ ion conduction. The glass network was stated to be formed of SiO₂ and P₂O₅ units, treated as SiO_{4/2} and 2POO_{3/2} groups. The silicate units are covalently bonded to phosphate units, resulting into variable electron densities of orthophosphoric units. The presence of Li₂O acts as a network modifier which influences Si-O-P linkages instead of Si-O-Si linkages, thereby forming a “noddle pipe” like structure for ion conduction [69]. The conductivity for 10Li₂O-70SiO₂-20P₂O₅ composition at 150 °C was reported to be $\sim 10^{-7}\ \Omega^{-1}\text{cm}^{-1}$. In another similar work on lithium phosphoborosilicate glasses by sol-gel process conductivity and modulus studies of the systems were explored thoroughly. Sample with composition of 10Li₂O-9P₂O₅-16.2B₂O₃-64.8SiO₂ was reported with a conductivity of $\sim 10^{-8}\ \Omega^{-1}\text{cm}^{-1}$ at 150 °C. These samples were found to be conductive above 150°C and exhibit a linear dependence with temperature [68].

1.5.3 A Novel Class of Systems: Ionogels

High conducting nature and wide electrochemical potential window of ILs attracts the electrochemists differently for their advance applications. Thus, ILs have been immobilized within the solid-porous matrices for applications in solid-ionic systems with better ionic conductivity and mechanical stability. In such composites, the host (solid matrix) provides the mechanical support and the space for the electrolytes through the connected pathways between the pores (pore size of nano-porous silica is $\sim 2.0 - 35\text{ nm}$) [80]. Present work also centres on Li⁺ ion containing silica-gel solid electrolytes that have been prepared with compositional alterations as well as by different preparation procedures. These systems are ionic in nature and their ionic conductivities exhibit

striking results and are compositional dependent. These silica-gel composites have been prepared with the aim of their usages as a potential electrolyte in solid-state devices.

Li^+ conducting IL confined silica gel composites were explored for their structure and properties by Wullen *et al.* through NMR studies. ^{29}Si NMR of the IL containing glass composites produce a single resonance peak at 110 ppm whereas, IL free glass composite exhibit three different signals at -91, -101 and -111 ppm. These signals can be assigned in terms of Q^n notation as Q^2 (-91 ppm), Q^3 (-101 ppm) and Q^4 (-110 ppm) for SiO_4 unit being connected to next SiO_4 unit by n number of bonds. The results confirm for formation of fully condensed glass network in presence of IL whereas in absence of IL presence of loose silicate with high residuals of Si-OH and Si-OC₂H₅ groups were noticed [73]. Dynamics of IL and Li^+ ion was also explored into the glass matrix by ^{19}F and ^7Li NMR studies. ^7Li NMR accounts for an increase in Li^+ ion mobility with increasing [BMIM] BF₄/LiTf ratio. ^{19}F NMR suggests about the restricted dynamics of triflate ions of IL with in the SiO₂ glass matrix irrespective of [BMIM] BF₄/LiTf ratio. Later, they explored the effect of organic fillers (eg. polyethylene oxide (PEO), ployphosphazene oxide (PPZ) and polyacrylonitrile (PAN)) in inorganic-organic hybrid electrolytes [75]. In one of such system, local Li^+ ion motif was analysed in (PEO)_n: LiTFSI composite and it was observed that for higher salt concentration (~80 wt% Li⁺ salt) these composites exhibit very good ionic conductivity and mechanical stability.

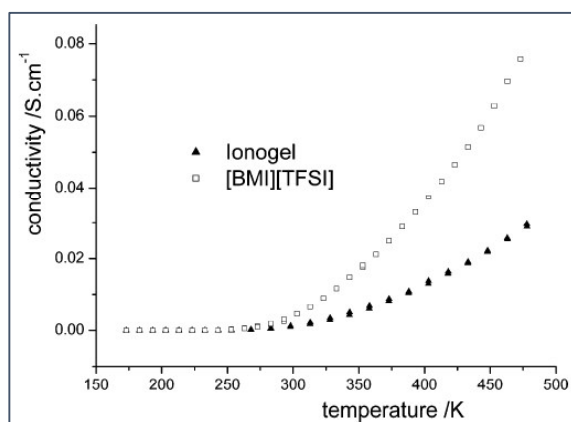


Fig. 1.11 Conductivity versus temperature for the pristine IL ([BMIM] TFSI) and a silica based ionogels ($x = 0.5$).

Néouze *et al.* reported for ionogels prepared through a non – aqueous sol-gel route, good thermal and mechanical stabilities and electrical conductivity of $\sim 10^{-2} \Omega^{-1}\text{cm}^{-1}$ at 227 °C.

Later, the same group reported ionogels where the IL: host molar ratio was up to 1:1, and the IL is confined in the host matrix with good thermal and solvent stability with a conductivity value of $\sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$ at room temperature similar to that of pure IL. These compositions do not have any small ions such as Li^+ . This high ionic conductivity was attributed to interconnected porosity present in the ionogels (Fig. 1.11). In another neutron scattering study in an IL confined matrix, the authors have indicated that dynamics of ions of IL slowed down compared to bulk IL [70-72].

Echelmeyer *et al.* attempted the confinement of IL in lithium-silicate network by sol-gel process and reported significant conductivity enhancement ($\sim 10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature) [73]. Here contribution of IL in conduction is justified based on diffusion coefficient of cations and anions. However, different preparations of the same compositions gave different absolute values for ionic conductivity and diffusion coefficients. Previous work by our group, on external dispersion of IL- [BMIM] BF_4 on the $\text{Li}_2\text{SO}_4\text{-Li}_2\text{O-P}_2\text{O}_5$ glass matrix resulted in increase in conductivity to certain orders (~ 5 orders) of magnitude [76]. According to Karout and Pierre, ionic liquids act as condensation catalysts of silica in gel to glass condensation and as a moderator of the condensation rate due to limitation of the dissolved species by diffusion [77]. These materials are of much interest as electrolytes in smart materials and various battery applications [78, 74].

1.5.4 Ionic Liquids and Their Nano - Confinement [80]

“Functionalized ionic liquids (FILs)” a new class of ionic liquids was discovered in 1998 for their diverse applications [81]. They have nature with melting point below 100°C [82 - 84]. Walden synthesized the first IL $[\text{EtNH}_3]\text{NO}_3$ with melting point 12°C in 1914 [85]. The high moisture sensitivity of ILs, prevented them to gain any attention. Later in 1992, Wilkes group produced air and water stable 1-ethyl-3-methylimidazolium based IL with different counterparts [86], with this, the field observed a major leap and now their usages have been extended.

ILs have bulky organic cations such as imidazolium, pyridinium, pyrrolidinium, quaternary ammonium or tetraalkylphosphonium with weak intermolecular interactions and low charge densities. This makes their solid state energetically less favourable to

exist in a regular lattice making them low melting salts or room temperature ILs. They exhibit good bulk conductivity at room temperature and this property gains the attention of electrochemists. However, their liquid state limits their usages in device applications. This problem was resolved by confining ILs in solid matrices. Confinement of ILs in nano pores of the solid matrices introduces a new class of hybrid systems with improved mechanical stability as well as the ionic conductivity. Different solid matrices that has been used for IL confinement are nano-porous silica and carbons, metal organic frameworks, covalent organic frameworks, carbon nanotubes and zeolites. The most fascinating properties of hybrid materials is their change in properties from those of bulk state. Another important finding is that the properties of these matrices can be tuned by varying the pore sizes, surface functionalities, loading fractions of the ILs etc. with a wider range of applications.

The confinement of ILs in nano-porous matrices mainly occurs in two different ways i.e. (i) covalent grafting, and (ii) physical confinement. It can be performed in three different ways, (i) *in-situ* introduction, (ii) post impregnation, and (iii) ship-in-bottle process. In the present thesis work, IL has been immobilized in novel silica-gel solid matrix by *in-situ* introduction (*vide infra*).

Covalent grafting of ILs: Covalent immobilization of ILs is attained by the chemical reaction between the silica pore wall and the imidazolium based ILs. Covalent confinement of ILs minimizes the need of IL in the matrix. The major drawback of the procedure is that the IL forms a self-assembly of a monolayer and becomes a part of solid support once it is bound to it. Thus, it no longer possesses the bulk-phase properties.

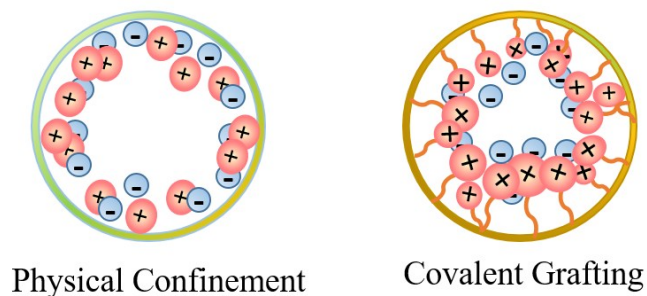


Fig. 1.12 Physical confinement versus covalent grafting of IL on solid matrix [80].

Physical confinement of ILs: Low vapour pressure of ILs significantly favours physical confinement with permanent coating onto the pore surface either by *in-situ* introduction or post impregnation. In this way, multilayers of ILs are immobilized onto the pore wall support, thereby retaining its bulk-phase properties largely.

1.5.5 Advance Applications of Confined IL Matrices

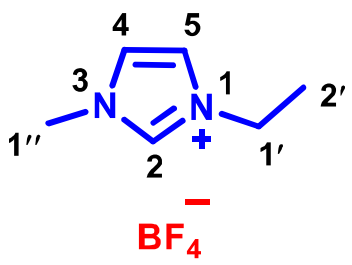
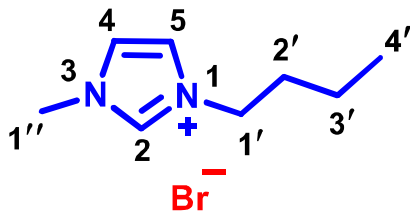
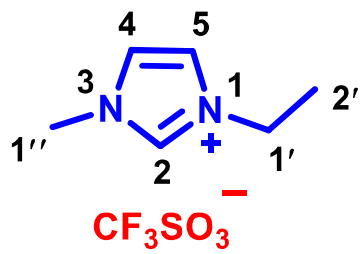
Ionic liquids in their bulk phase are very much different from the confined ILs. The confinement of ILs into different host matrices has increased the overall potentials of both the host matrices as well as the ILs. Such systems find their promising applications in catalysis, variable sensors and separators, ionogels, supercapacitors, carbonization and lubricants [80, 87-89].

Despite of advance applications of confined ILs in both fundamental and applied research, they still exhibit many challenges, some of them are listed as follows:

- (i) It is difficult to understand the structure and properties of confined IL systems.
- (ii) Theoretical dimensions for confinement of ILs in solids matrices in multiple layer is difficult to achieve.
- (iii) It is difficult to understand the effect of presence of impurities and the interactions of ILs with other trapped molecules.
- (iv) Understanding about the increase in potential of functionalized ILs on confinement in solid matrices, which can be later tuned for their catalytic activities and selectivity.
- (v) Electrochemical properties of the nano confined ILs, their structure and dynamical properties needs thorough investigations.

In the present work three different ILs has been explored. Structure and physical properties of these ILs have been in Table 1.4.

Table 1.4 Structure and physical properties of ILs

Name and Structure	Physical Properties
1-ethyl-3-methylimidazolium tetrafluoroborate 	Molecular Weight 197.97 m.p. 15 °C b.p. > 350 °C Density 1.294 g/ml
1-butyl-3-methylimidazolium bromide 	Molecular weight 219.15 g/mol m.p. 65-75 °C b.p. > 250 °C Density 1.287 g/ml
1-ethyl-3-methylimidazolium trifluoromethanesulfonate 	Molecular weight 260.23 m.p. 15 °C b.p. > 350 °C Density 1.387 g/ml

1.6 Applications of Fast Ionic Systems: Supercapacitors

Challenges of global warming and environmental destruction has focused on eco-friendly power sources. In order to store high electric energy and deliver the same. To meet this requirement, supercapacitors (SCs) with high capacitance and sufficiently long lifetime are needed. Generally, there are three types of supercapacitors based on charging discharging processes at the electrode-electrolyte interfaces [94]. These are namely (a) Electrochemical Double Layer (EDLC), (b) Pseudo capacitor, and (c) Hybrid type (a hybrid form of EDLC and pseudo capacitor) capacitor.

Thermal instability of electrolytes and organic polymer separators make them unsuitable for the capacitor applications, which requires high temperature applications. In fabrication of capacitors, a separator plays an important role in ion migration. Polymers, cellulose paper, fabrics etc. anything which does not allow mass transfer from one electrode to another electrode. Carbonaceous materials, pseudocapacitive metal oxides, conducting polymers and their composites or high voltage stable organic electrolytes have been used for high performance electrodes. Porous carbon-based materials are most common for EDLCs, as they exhibit high specific surface area (active) and excellent physicochemical stability.

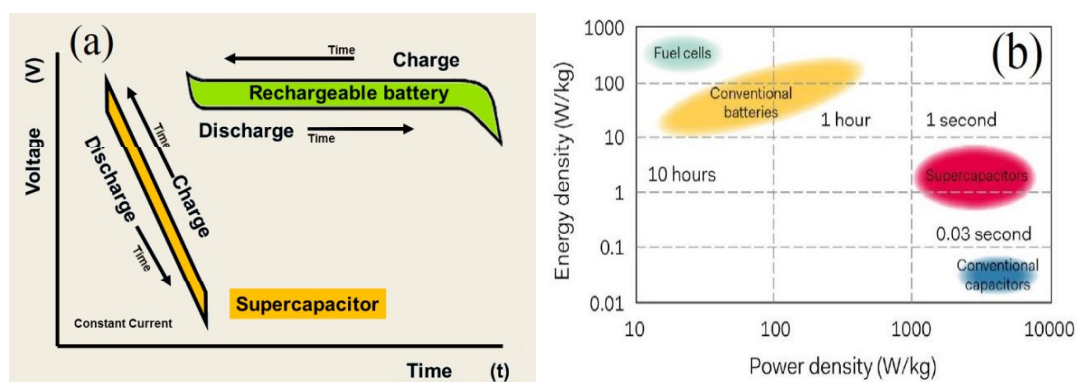


Fig. 1.13 Energy and power density comparison of a battery and a supercapacitor.

Supercapacitors (SCs) with electrochemical behavior have a battery like configuration. It is composed of bi-electrode configuration, separated by a separator immersed in an electrolyte. They store energy based on a simple charging-discharging process at electrode-electrolyte interfaces. Energy stored in supercapacitors is in a range of 100 - 1000 F whereas a conventional capacitor stores energy only in a range of mF or μ F [91, 92]. Thus, SCs are distinguished from conventional capacitors in terms of high surface area electrodes with higher capacitor magnitudes. These can be employed either with any battery or cell or independently when used in electrical vehicles. They exhibit certain advantages over other traditional energy storing devices. Some of these are (i) number of charging-discharging cycles, (ii) high power capacity, (iii) wide thermal operating range, and (iv) most importantly these can be recharged very quickly and can release a large amount of power in comparison to conventional batteries [93, 94]. The energy storage mechanism in these devices is based on the following principles [91]:

- (i) The EDLC stores energy due to adsorption of Coulombian charge near the electrode-electrolyte interface.
- (ii) Pseudo capacitor stores energy owing to superficial redox reactions correlated to their respective potential.
- (iii) While collaboration of both forms the storage principle of the hybrid supercapacitor.

1.6.1 Applications of Supercapacitors

Demand for high-energy storage device applications regarding electronic portability to hybrid electric vehicles has led to a constant increase in applications of supercapacitors. However, this sector needs to work further for device optimization and cost reduction [95]. Some of the fields that where supercapacitor applications could be observed in field of viz., (i) public sector applications, (ii) automobile and transport applications, (iii) defence and military applications, (iv) computer and memory chips, (v) medical and industrial applications etc. [90].

1.6.2 Status and Future Challenges

High energy density with the long-term stability of hybrid supercapacitors defines the practical applications of supercapacitors especially hybrid supercapacitors in energy storage device applications. The only limitation for this is the availability of a critical power source. This major drawback can be subsided by designing the whole unit of supercapacitors in an array of separated electrochemical cells with same plane fabrication. Such configuration provides control over the current and voltage output [90]. However, the parameter required to tune the performing of supercapacitors further needs thorough innovations and design.

1.7 Gaps in Existing Research

The field amorphous/glassy systems have been explored in a huge quantity for their structure and outstanding properties. Randomness in their atomic arrangements attracts the material pioneers for their usages in variable device applications. All these efforts are tremendous and have their own importance. Two distinguished area have been explored in this thesis work i.e. (i) lead oxyhalide glasses, and (ii) sol-gel derived silica ionogels.

-
- (i) An enormous amount of research has been done to understand the structure of lead halide/ lead oxyhalide glasses with other glass formers such as P_2O_5 , B_2O_3 , SiO_2 etc. The literature helps in understanding the structure of these glasses very well. As far to our understanding, there is no study regarding the relations between the statistical distribution of bonding or related parameters and properties of glasses such as glass transition temperature, electrical conductivity, density, magnetic nature etc. A systematic correlation in between their structural parameters and properties always lacks.
 - (ii) Similarly, silica derived glasses are yielded at very high temperature (≥ 1000 °C) and exhibit very poor conductivity ($\sim 10^{-7} - 10^{-10} \Omega^{-1}cm^{-1}$). A decade ago, ionogels gained a sudden attention for their high ionic conductivity ($\sim 10^{-3} - 10^{-4} \Omega^{-1}cm^{-1}$). These composites although exhibit high ionic conductivity but, their solid state of the composites has been compromised.
 - (iii) Another finding states that these systems have been either explored for only IL conduction in confined matrices or a Li^+ and IL conduction, in these cases application of such composite to device applications has not been explored properly. Such systematic investigation of conductivity-structural correlations in thermally stable and unstable region may lead to better understanding of these composites.
 - (iv) IL confined in silica matrices (for ionogels) is in large amount. In such systems, IL has been trapped in the pores of silica pore size and it contributes to conductivity.
 - (v) Confinement in a very small amount and into the nanopore still needs a good investigation, where the Li^+ ions from the host matrix should be encouraged to contribute in electrical transport. In a way, it is required to explore composites where IL is practically immobilized, but it facilitates Li^+ ion transport. So, small IL confined systems have not been investigated properly.
 - (vi) Mechanism of electrical transport particularly where the salt ions of host matrix are likely to contribute in conductivity and has not got any attention. Thus, needs thorough investigations.
-

1.8 Statement and Objective of the Work

Vitreous and disordered structure of amorphous composites is the main reason why the pioneers look for the possibility of fast ionic conduction in them. Li^+ fast ionic glasses are the most explored but their poor ionic conductivity at room temperature, limits their usages for devices applications. But still they are of immense interest due to their complex structure, wide glass forming region and interesting electrical transport studies in a wide temperature range. The present thesis focuses on a systematic understanding of high temperature structural and electrical transport properties particularly in thermally stable region of the ionic glasses and silica gels.

Objectives of the thesis are:

- (i) To synthesize IL confined Li based silica gels.
- (ii) IL confinement in various matrices of silica gel composites without compromising their solid-state.
- (iii) To understand the mechanism of electrical conductivity in these systems.
- (iv) Structural and thermal characterization of the prepared ionogels.
- (v) To understand the electrical conductivity phenomenon and the effect of change in concentration of ILs as well as charge carriers.
- (vi) To explore and understand the mixed alkali (Li^+ and K^+ ion based systems) effect in ionogels.
- (vii) To explore their application as a solid electrolyte for solid-state device applications (supercapacitors).

In order to achieve these objectives a simple $\text{SiO}_2\text{-Li}_2\text{O-CuCl}_2$ system has been chosen for investigations. We know $\text{SiO}_2\text{-Li}_2\text{O}$ system is ionic in nature although it still shows very poor conductivity ($\sim 10^{-9} - 10^{-10} \Omega^{-1} \text{cm}^{-1}$). This very simple system was chosen to explore the structural and conducting properties by making silica ionogels. In these ionogels we do not compromise with the solid state of the matrix. Three different ILs were chosen for the present thesis namely, (i) 1-Butyl-3-imidazolium bromide [BMIM] Br, (ii) 1-Ethyl-3-imidazolium tetrafluoroborate [EMIM] BF_4 , and (iii) 1-Ethyl-3-imidazolium trifluoromethanesulphonate [EMIM] CF_3SO_3 . These ILs have been confined into the silica gel matrices by hydrolytic and non-hydrolytic processes. [EMIM] BF_4 derived composites has also been explored for mixed alkali effect.

Literature findings on non-hydrolytic synthesized ionogels showed good electrical conductivities of $\sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$ at room temperature where the IL: host molar ratio was up to 1:1. These compositions do not have any small ions such as Li^+ . This high ionic conductivity was attributed to the dynamics of IL anion and cation in the interconnected porosity present inside the ionogels [70-72]. In another attempt of IL confinement in lithium-silicate network by sol-gel process reported a significant conductivity enhancement ($\sim 10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature) [73]. The high conductivity of the composites was justified based on the diffusion coefficient of cations and anions.

Previous work by our group, on external dispersion of IL-[BMIM] BF_4 on the Li_2SO_4 - $\text{Li}_2\text{O-P}_2\text{O}_5$ glass matrix also resulted in increase in conductivity to certain orders of magnitude [76]. These studies indicates that the confinement of IL in the solid matrix enhances the electrical transport and these materials are of much interest as electrolytes in smart materials and various battery applications [78, 79].

References

1. *The Gaurdian*, Science, “Nobel prize in chemistry awarded for work on lithium-ion batteries.” 2019.
 2. Rao K. J., “Structural Chemistry of Glasses”. Elsevier, 2002.
 3. Goldschmidt V. M., Barth T., Lunde G., Zachariassen W. H., “Geochemical distribution law of the elements. VII. Summary of the chemistry of crystals.” *Skr. Nor. Vidensk. Akad* **1** (1926) 1-117.
 4. W. H. Zachariassen, “The atom arrangement in glass.” *Journal of the American Chemical Society*. **54** (1932) 3841 – 3851.
 5. Michael Faraday, “On electro-chemical decomposition” Royal Society, 1833.
 6. Harry L. Tuller, Peter K. Moon, “Fast ion conductors: Future trends.” *Materials Science and Engineering: B*. **1** (1988) 171-191.
 7. Arnold Lud’en, “Cation transport mechanisms in high temperature rotor phases of sulfates.” *Journal of Solid-State Chemistry* **107** (1993) 296-298.
 8. Huggins R. A., “Recent results on lithium ion conductors.” *International Symposium on Solid Ionic and ionic-Electronic Conductors*. Elsevier 1977, 773-781.
 9. D. Ravaine, “Ionic transport properties in glasses.” *Journal of Non-Crystalline Solids* **73** (1985) 287-303.
 10. C. C. Liang, “Conduction Characteristics of the Lithium Iodide-Aluminum Oxide Solid Electrolytes.” *Journal Electrochemical Society* **120** (1973) 1289-1292.
 11. Peter V. Wright, “Polymer electrolytes – The early days.” *Electrochimica Acta* **43** (1998) 1137-1143.
 12. U. M. Gundusharma, Charles MacLean, E. A. Secco, “Rotating sulfate ion contribution to electrical conductivity in Li_2SO_4 and LiNaSO_4 .” *Solid State Communications* **47** (1986) 479-481.
 13. S. Chandra, “*Superionic Solid: Principle and Application*” North Holland Publishing Company, Amsterdam (1981).
 14. Yoshiyuki Inaguma, Chen Liqun, Mitsuru Itoh, Tetsuro Nakamura, “High ionic conductivity in lithium lanthanum titanate.” *Solid State Communication* **86** (1993) 689-693.
-

-
15. H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, "Ionic conductivity of the lithium titanium phosphate ($\text{Li}_{1+x}\text{M}_x\text{Ti}_2/(\text{PO}_4)_3$, M=Al, Sc, Y, and La) systems." *Journal of Electrochemical Society* **136** (1989) 590.
 16. Klaus Otto, M. E. Milberg, "Ionic conduction in alkali and thallium silicate glasses." *Journal of the American Ceramic Society* **51** (1968) 326-329.
 17. M. Tatsumisago, T. Minami, M. Tanaka, "Lithium ion conducting glasses prepared by rapid quenching." *Material Chemistry and Physics* **18** (1987) 1-17.
 18. Lee C. H., Joo K. H., Kim J. H., Woo S. G., Sohn H. J., Kang T., Park Y., Oh J. Y., "Characterizations of a new lithium ion conducting $\text{Li}_2\text{O}-\text{SeO}_2-\text{B}_2\text{O}_3$ glass electrolyte." *Solid State Ionics* **149** (2002) 59.
 19. Deshpande A. V., Deshpande V. K., "Correlation of glass transition temperature and density with electrical conductivity of lithium sulfoborosilicate glasses." *Solid State Ionics* **177** (2002) 2747-2751.
 20. Gandhi P. R., Singh K., "Conductivity enhancement in Li_2SO_4 incorporated $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ glass system." **36** (1989) 97-102.
 21. Soman S., Iwai Y., Kawamura J., Kulkarni A. R., "Isothermal crystallization and effect of soak time on phase evolution, microstructure and ionic conductivity of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$ glass-ceramic." *Journal of Solid State Electrochemistry* **439** (2016) 38-45.
 22. Akitoshi Hayashi, Hideki Morishima, Kiyoharu Tadanaga, Masahiro Tatsumisago, "Characterization of Solid Electrolytes Prepared from Ionic Glass and Ionic Liquid for All-Solid-State Lithium Batteries." *Solid State Ionics* **192** (2011) 126-129.
 23. Lévassieur Alain, Brethous Jean-Claude, Kbala Mohamed, Hagenmuller Paul, "Synthesis and characterization of new amorphous solid electrolytes." *Solid State Ionics* **5** (1980) 651-654.
 24. Singh K., Rokade S., "Electrical conductivity of a new solid electrolyte glass material $\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$." *Journal of Power Sources* **13** (1984) 151-158.
 25. Alexander Grayson M., Riley Brian, "Ion conducting glasses in the $\text{Na}_2\text{O}-\text{Y}_2\text{O}_3-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{Y}_2\text{O}_3-\text{SiO}_2$ systems." *Solid State Ionics* **18-19** (1986) 478-482.
-

26. Tatsumisago Masahiro, Hama S., Hayashi A., Moromoto H., Minami T., "New lithium ion conducting glass-ceramics prepared from mechanochemical $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass." *Solid State Ionics* **154-155** (2002) 635-640.
27. Tatsumisago Masahiro, "Glassy materials based on Li_2S for all-solid-state lithium secondary batteries." *Solid State Ionics* **175** (2004) 13-18.
28. B. V. R. Chowdari, S. K. Akhter, "Ionic transport studies of lithium phosphoarsenate glassy system." *Solid State Ionics* **28-30** (1988) 747-751.
29. B. V. R. Chowdari, K. L. Tan, W. T. Chia, R. Gopalkrishnan, "Thermal, electrical and structural characterization of $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{MoO}_3$ glasses." *Solid State Ionics* **40-41** (1990) 684-688.
30. Nobuya Machida, Kazuko Fuji, Tsutomu Minami, "Preparation and ionic conductivity of rapidly quenched glasses in the system $\text{Li}_2\text{O}-\text{TiO}_2-\text{P}_2\text{O}_5$." *Chemistry Letters* **3** (1991) 367-370.
31. S. Hazra, S. Mandal, A. Ghosh, "Properties of unconventional lithium bismuthate glasses." *Physical Review B* **56** (1997) 8021-8025.
32. Munia Ganguli, K. J. Rao, "Structural role of PbO in $\text{Li}_2\text{O}-\text{PbO}-\text{B}_2\text{O}_3$ glasses." *Journal of Solid State Chemistry* **145** (1999) 65-76.
33. Issac Abrahams, Emina Hadzifejzovic, "Lithium ion conductivity and thermal behavior of glasses and crystallized glasses in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$." *Solid State Ionics* **134** (2000) 249-257.
34. Young-Il Lee, Jong-Heun Lee, Seong-Hyeon Hong, Youngsin Park, "Li-ion conductivity in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{V}_2\text{O}_5$ glass system." *Solid State Ionics* **175** (2004) 687-690.
35. C. H. Lee, K. H. Joo, J. H. Kim, S. G. Woo, H. J. Sohn, T. Kang, Y. Park, J. Y. Oh, "Characterization of a new lithium ion conducting $\text{Li}_2\text{O}-\text{SeO}_2-\text{B}_2\text{O}_3$ glass electrolyte." *Solid State Ionics* **149** (2002) 59-65.
36. N.K. Karan, B. Natesan, R.S. Katiyar, "Structural and lithium ion transport studies in borophosphate glasses." *Solid State Ionics* **177** (2006) 1429-1436.
37. Kang Ill Cho, Sun Hwa Lee, Dong Wook Shin, Yang Kuk Sun, "Relationship between glass network structure and conductivity of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ electrolyte." *Electrochimica Acta* **52** (2006) 1576-1581.

-
38. Benson K. Money, K. Hariharan, "Glass formation and electrical conductivity studies of melt quenched and mechanically milled $50\text{Li}_2\text{O}:(50-x)\text{P}_2\text{O}_5:x\text{B}_2\text{O}_3$." *Solid State Ionics* **179** (2008) 1273-1277.
 39. Benson K. Money, K. Hariharan, "Crystallization kinetics and phase transformation in superionic lithium metaphosphate ($\text{Li}_2\text{O}-\text{P}_2\text{O}_5$) glass system." *Journal of Physics and Condensed Matters* **21** (2009) 115102.
 40. Poonam Sharma, Dinesh Kumar Kanchan, Meenakshi Pant, K Padmasree, "Transport properties of super ionic $\text{AgI}-\text{Ag}_2\text{O}-\text{V}_2\text{O}_5-\text{TeO}_2$ glasses." *Indian Journal of Pure and Applied Physics* **48** (2010) 39-46.
 41. R. S. Muralidharan, R. V. Anavekar, "Ion transport studies on $\text{Li}_2\text{O}-\text{PbO}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glass system." *IOP Conference Series: Material Science and Engineering* **2** (2009) 012056.
 42. Prashant Dabas, K. Hariharan, "Thermoanalytical, structural and ionic conductivity studies on $50\text{Li}_2\text{O}-45\text{P}_2\text{O}_5-5\text{Nb}_2\text{O}_5$ glass." *Solid State Ionics* **225** (2012) 641-644.
 43. G. Delaizir, V. Seznec, P. Rozier, C. Surcin, P. Salles, M. Dolle, "Electrochemical performances of vitreous materials in the system $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$ as electrode for lithium batteries." *Solid State Ionics* **237** (2013) 22-27.
 44. Prashant Dabas, K. Hariharan, "Nucleation and crystallization kinetics of rapidly quenched lithium pyrophosphate glass." *Solid State Ionics* **243** (2013) 42-49.
 45. Benson K. Money, K. Hariharan, "Mixed alkali effect on crystallization kinetics of $x\text{Na}_2\text{O}:(50-x)\text{Li}_2\text{O}:50\text{P}_2\text{O}_5$." *Solid State Ionics* **262** (2014) 824-828.
 46. Satwinder Singh, Gaurav Kalia, K. Singh, "Effect of intermediate oxide (Y_2O_3) on structural and optical properties of lithium borosilicate glasses." *Journal of Molecular Structure* **1086** (2015) 239-245.
 47. N. S. Saetova, A. A. Raskovalov, B. D. Antonov, T. V. Yaroslavtseva, O. G. Reznitskikh, N. I. Kadyrova, "The influence of lithium oxide concentration on the transport properties of glasses in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system." *Journal of Non-Crystalline Solids* **443** (2016) 75-81.
 48. S. Ibrahim, M. A. Marzouk, G. M. El Komy, "Structural characterization and electrical conductivity of vanadium-doped lithium ultraphosphate glasses." *Silicon* **9** (2017) 403-410.
-

-
49. Neelakshi Sharma, Anshuman Dalvi, "Dispersion of $\text{Li}_2\text{SO}_4\text{-LiPO}_3$ glass in $\text{LiTi}_2(\text{PO}_4)_3$ matrix: Assessment of enhanced electrical transport." *Journal of Alloys and Compounds* **782** (2019) 288-298.
 50. Neelakshi Sharma, Anshuman Dalvi, " Li^+ NASICON nanocrystallites in ionic glasses: A potential nano composite system for all solid-state Li^+ ion batteries." *AIP Conference Proceedings* **2115** (2019) 030550.
 51. O. L. Anderson, D. A. Staurt, "Calculation of activation energy of ionic conductivity in silica glasses by classical methods." *Journal of American Ceramic Society*. **37** (1954) 573-580.
 52. Christensen R., Olson G., Martin S. W., "Ionic conductivity of mixed glass former $0.35\text{Na}_2\text{O}+0.65[\text{x}\text{B}_2\text{O}_3+(1-\text{x})\text{P}_2\text{O}_5]$ glasses." *Journal of Physical Chemistry B* **117** (2013) 16577-16586.
 53. Ingram M., Mackenzie M. A., Muller W., Torge M., "Cluster and pathways: A new approach to ion migration in glass." *Solid State Ionics*. **28** (1988) 677-680.
 54. Ingram M. D., "Ionic conductivity and glass structure." *Philosophical Magazine B*. **60** (1989) 729-740.
 55. Goodman C. H. L., "Strained mixed-cluster model for glass structure." *Nature* **257** (1975) 370-372.
 56. Tachez M., Mercier R., Malugain J. P., "Quasielastic and inelastic neutron scattering from $\text{AgPO}_3\text{-AgI}$ glass." *Solid State Ionics* **20** (1986) 93-98.
 57. Rocca F., Delba G., Fornasini P., Tomasi A., "Structural study of $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$ glasses by X-ray absorption spectroscopy." *Solid State Ionics* **53-56** (1992) 1253-1259.
 58. Benasai P., Fontana A., Rodrigues P. A. M., "Light scattering in superionic glasses $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$: Brillouin and Raman Scattering." *Physics Review B*. **43** (1991) 1756-1762.
 59. Minami T., "Fast ion conducting glasses." *Journal of Non-Crystalline Solids*. **79** (1986) 367-381.
 60. Brinker C. J., Scherer G. W., "Sol-gel science: The Physics and The Chemistry of Sol-Gel Processing." Academic Press 2013.
-

-
61. Rosaria Ciriminna, Alexandra Fidalgo, Valerica Pandarus, Francois Beland, Laura M. Iiharco, Mario Pagliaro, "The sol-gel route to advanced silica based materials and recent applications." *Chemical Reviews* **113** (2013) 6592–6620.
 62. Sharp K. G., "A two-component, non-aqueous route of silica gel." *Journal of Sol-gel Science and Technology*. **2** (1994) 35-41.
 63. Vioux A., "Non-hydrolytic sol-gel routes to oxides." *Chemistry of Materials*. **9** (1997) 2292-2299.
 64. Larry L. H., West J. K., "The sol-gel process." *Chemical Review* **90** (1990) 33-72.
 65. Levy D., "Photochromic sol-gel materials." *Chemistry of Materials*. **9** (1997) 2666-2670.
 66. Yamane M., Hiroshi K., Yasumori A., Takahashi T., "Preparation of Pb-containing glass by the sol-gel process, reduction of Pb-migration during drying." *Journal of Non-Crystalline Solids*. **99** (1988) 160-167.
 67. Rubio F., Rubio J., Oteo J., "Effect of reaction parameters on the hydrolysis of zirconium propoxide - A study by infrared spectroscopy." *Journal of Materials Science Letters*. **17** (1998) 1839-1842.
 68. P. Muralidharan, Satyanarayana N., Venkateswarlu M., "Structural, ac Conductivity and Electric Modulus Studies of Lithium Based Quaternary Silicate Glasses Synthesised by the Sol-Gel Route." *Physics and Chemistry of Glasses* **46** (2005) 293-301.
 69. K. J. Rao, Baskaran N., Ramakrishnan P., Ravi B., Karthikeyan A., "Structural and Lithium Ion Transport Studies in Sol-Gel Prepared Lithium Silicophosphate Glasses." *Chemistry of Materials* **10** (1998) 3109-3123.
 70. M.-A. Néouze, Le Bideau J., Gaveau P., Bellayer S., Vioux A., "Ionogels, New Materials Arising from the Confinement of Ionic Liquids within Silica-Derived Networks." *Chemistry of Materials* **18** (2006) 3931-3936.
 71. M.-A. Neouze, Bideau J. L., Leroux F., Vioux A., "A Route to Heat Resistant Solid Membranes with Performances of Liquid Electrolytes." *Chemical Communications* (2005) 1082-1084.
-

-
72. J. Le Bideau, Gaveau P., Bellayer S., Neouze M.-A., Vioux A., "Effect of Confinement on Ionic Liquids Dynamics in Monolithic Silica Ionogels: 1H-NMR Study." *Physical Chemistry Chemical Physics* **9** (2007) 5419-5422.
73. T. Echelmeyer, Meyer H. W., van Wüllen L., "Novel Ternary Composite Electrolytes: Li⁺ Ion Conducting Ionic Liquids in Silica Glass." *Chemistry of Materials* **21** (2009) 2280-2285.
74. C. V. Cerclier, Zanotti J.-M., Le Bideau J., "Ionogel Based on Biopolymer-Silica Interpenetrated Networks: Dynamics of Confined Ionic Liquid with Lithium Salt." *Physical Chemistry Chemical Physics* **17** (2015) 29707-29713.
75. Q. Wang, Y. F. Nie, X. Y. Chen, Z. H. Xiao, Z. J. Zhang. Controllable synthesis of 2D amorphous carbon and partially graphitic carbon materials: Large improvement of electrochemical performances by the redox additive of sulfanilic acid azochromotrop in KOH electrolyte. *Electrochimica Acta* **200** (2016) 247 – 258.
76. Munesh Rathore, Anshuman Dalvi, Anil Kumar, W. Slubowska, J. L. Nowinski, "Ionic liquid dispersed Li⁺ ion oxide glasses and glass ceramics: Assessment of electrical transport and thermal stability." *Solid State Ionics* **282** (2015) 76-81.
77. Karout A, Pierre Ac, "Silica gelation catalysis by ionic liquids." *Catalysis Communications*. **10** (2009) 359-361.
78. N. Gil-González, Akyazi T., Castaño E., Benito-Lopez F., Morant-Miñana M., "Elucidating the Role of the Ionic Liquids in the Actuation Behavior of Thermo-Responsive Ionogels." *Sensors and Actuators B: Chemical* **260** (2017) 380-387.
79. J. Le Bideau, Viau L., Vioux A., "Ionogels, Ionic Liquid Based Hybrid Materials." *Chemical Society Reviews* **40** (2011) 907-925.
80. Zhang S, Zhang J, Zhang Y, Deng Y, "Nanoconfined Ionic Liquids." *Chemical Reviews*. **110** (2017) 6755-6833.
81. Plechkova N. V.; Seddon, K. R., "Applications of ionic liquids in the chemical industry." *Chemical Society Reviews*. **37** (2008) 123-150.
82. Wilkes J. S., "A short history of ionic liquids-from molten salts to neoteric solvents." *Green Chemistry*. **4** (2002) 73-80.
-

-
83. Marsh K. N., Boxall J. A., Lichtenthaler R., "Room temperature ionic liquids and their mixtures - A review." *Fluid Phase Equilibria*. **219** (2004) 93-98.
84. Hallett J. P., Welton T., "Room temperature ionic liquids: solvents for synthesis and catalysis. 2" *Chemical Reviews*. **111** (2011) 3508-3576.
85. Walden P., "On the molecular size and conductivity of some molten salts." *Bulletin of Academy of Imperial Sciences.(St. Petersburg)* **8** (1914) 405-422.
86. Wilkes J. S., Zaworotko M. J., "Air and water stable 1-Ethyl-3-methylimidazolium based ionic liquids." *Journal of the Chemical Society, Chemical Communications* (1992) 965-967.
87. Hallett J. P., Welton T., "Room-temperature ionic liquids: solvents for synthesis and catalysis." *Chemical reviews*. **111** (2011) 3508-3576.
88. Bazant M. Z., Storey B. D., Kornyshev A. A., "Double Layer in Ionic Liquids: Overscreening versus Crowding." *Physical Review Letters*. **106** (2011) 046102.
89. Lawrenson S., North M., Peigneguy F., Routledge A., "Greener solvents for solid-phase synthesis." *Green Chemistry*. **19** (2017) 952-962.
90. S. R. C. Vivekchand, C. S. Rout, K. S. Subrahmanyam, A. Govindaraj, C. N. R. Rao., "Graphene-based electrochemical supercapacitors." *Journal of Chemical Sciences* **120** (2008) 9 – 13.
91. A. Muzaffar, M. B. Ahamed, K. Deshmukh, J. Thirumalai. "A review on recent advances in hybrid supercapacitors: Design, fabrication and applications." *Renewable and Sustainable Energy Reviews* **101** (2019) 123-145.
92. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna. "Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer." *Science* **313** (2006) 1760-1763.
93. R. Kotz, M. Carlen. "Principles and applications of electrochemical capacitors." *Electrochimica Acta* **45** (2000) 2483–2498.
94. M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff. "Graphene based ultra-capacitors." *Nano Letters* **8** (2008) 3498–3502.
95. Andrea Balducci, Ugo Bardi, Stefano Caporali, Marina Mastragostino, Francesca Soavi, "Ionic liquids for hybrid supercapacitors" *Electrochemistry Communications* **6** (2004) 566 – 570.
-



This document was created with the Win2PDF “print to PDF” printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>