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An Overview of Fast Ion Conductors

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Abstract- Fast ion conductors are considered to have great potential in the field of science and technology to create avenues in energy storage and conversion process. However, it is not yet known why only a few materials can supply remarkably higher ionic conductivity than typical solids or how one can design super-ionic conductors following simple procedures. Analysing the past studies, here I have put emphasis on the origin, classification, preparation, and applications of super-ionic conductors. The studies show that fast diffusion in fast ion conductors does not occur through isolated ion hopping as is typical in solids, but instead proceeds through concerted migrations of multiple ions with low energy barriers. Furthermore, I clarify that the low energy barriers of the concerted ionic diffusion are a result of exceptional mobile ion configurations and firm mobile ion interactions in fast ion conductors. This review provides best possible route to understand the concept and mechanism of super-ionic conductors which can pave way for universal strategy to design solid materials into fast ion conductors.

Keywords- Super-ionic conductors; Solid-state reaction; X-ray diffraction; Impedance spectroscopy; Ionic conductivity; Sensors.

I. INTRODUCTION

The solids which exhibit an unusually high ionic conductivity at ambient temperature are known as the super-ionic conductors (SICs) or fast ion conductors (FICs) .They are sometimes refered to as solid electrolytes (SEs) [1,2]. Their wide applications in micro batteries, sensors, smart devices etc. force many investigators to study their properties in order to produce improved materials [3]. Their structure is characterized by strong disorder in the sublattice [4]. The specific conductivity (**o**) usually ranges from 10-3 to 10 Siemens per centimetre . These values are usually very high for a normal crystalline solid , but may be lower than many electronic conductors such as metals, which have σ range from 10 to 105 S cm-1. Thus, the superionic conductors are intermediate between normal crystalline solids with 3- dimentional structures and immobile ions, and liquid electrolytes, which do not have regular structures

but have mobile ions. The general principles for effective superionic conduction are straight forward: (1) It must be possible for the mobile ion to move between lattice sites . This usually means that a smaller ion will move via the static sublattice of larger ions .Thus, superionic conductors tend to involve small cations such as Ag+, Cu+, H+, Li+, although highly polarizable larger anions may also give rise to significant ionic conductivity (eg. F-or O2-).

(2) In a crystal, large number of ions of one species should be mobile (i.e., large value of n in equation, $\sigma = ne\mu$); where, e is electronic charge and μ is the mobility of ions. (3) The ion movement must be macroscopic. The structure must have a fully connected network of lattice sites accessible to the mobile ions with low energy barriers between them [5]. (4) The mobility is enhanced if there are more vacant sites for the conducting ion than there are ions to fill them, thus reducing the effect of ions

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blocking other ions [6]. This, is facilitated either by a vessel from that period, which was found in the structure with an inherently large number of sites per mobile ion (such as α -Aql, whose structure is having six tetrahedral sites per mobile cation), or by the formation of intersititial defects (e.g., β-PbI2, whereby mobile anions move between sites through voids within the fluorite structure).

SICs have significant importance in various devices such as solid state electrochemical cells, sensors, fuel cells and oxygen concentration cells. One of the indispensable applications of SICs as solid electrolytes is in batteries because of their long life, high energy density, and minimum leakage that make them advantageous and preferable over liquid electrolytes. Other types of cells that are finding applications are miniature primary cells which operate at room temperature and which have a long life rather than a high power output .These are used in electronic watches, heart pacemakers and in military applications [4,7].



Fig.1. Glass vessel found in the tomb of the Egyptian king Tutmosis III [8].

The first objects of glass produced by men date back to about 7000 B.C. and were found in Egypt and Mesopotamia. About 1500 B.C. the first glassware was produced. Fig.1. shows a beautiful glass

tomb of the Egyptian king Tutmosis III [8]. The technique was simple. A nucleus of clay and sand was formed and fibres of the glass melt were rolled around this nucleus. After cooling down, the nucleus was removed, and a vessel of glass, like the one in the figure, was created.

Solid electrolytes were first discussed by Faraday at the end of 19th century [9] .The study of ionic conduction in solid state originated way back in 1836 when Faraday discovered that β -PbF2 and Ag2S are good conductors of electricity [10] .These solids are the first ever discovered solid electrolytes. In 1851, Hittrof investigated the conductivity of Ag2S and Cu2S and concluded from decomposition during the current flow that an electrolytic conduction mechanism exist in these materials [11] .The discoveries of good Na+ mobility in glass by Warburg [12] as well as the first transference number measurements by Warburg and Tegetmeimer [13] are important contributions in the study of solid ionic conductors. Katayama [14] in 1908 demonstrated that fast ionic conduction can be made use of in potentiometric measurements. The first major discovery using superionic conductors was made when German Nobel Laurate Nernst invented a lighting device using ytteria (YO2) stabilized zirconia (ZrO2) in 1900 [15]. Tubandt and Lorenz, in 1914, investigated silver and thalium halides and noticed remarkably high conductivity of α -phase of AgI [16] . In 1960s, silver ion conducting solids such as Ag3SI [17] and Ag4MI5 (M = Rb, K, NH4) [18,19] were discovered. The use of Ag3SI by Takahashi and Yamamoto [20], RbAg4KI5 by Arque and Owens [21] and Aq4KI5 by Chandra et al [22] in electrochemical cells were demonstrated soon after this. In 1978, Takahashi et al [23] discovered a room temperature superionic conducting phase in the system RbCl-CuCl-CuI which shows Cu+ ionic conductivity equal to 0.40 Scm-1 at room temperature. The structure of the phase was investigated by Geller et al [24] and was given the formula RbCu4Cl3l2. The most important discovery was *B*-alumina by Kummer et al, which has triggered the area of research with an optimum approach in the field of solid state ionics [25]. Since

then various kinds of solid conductors such as cation conductors, anion conductors, oxide ion conductors, etc., have been found to have high conductivity at various temperatures in crystal, polycrystalline and glass phase. Past two decades, high ionic conductors have also been found in polymeric forms and composite forms, i.e., dispersing insulating materials in ionic solids [26]. These different kinds of FICs with diverse phases are being synthesized to meet the practical requirements and conditions.

The common features of FIC materials are : (a) crystal bonding is ionic in nature, (b) electrical conductivity is high (10-1 to 10-4 Scm-1), (c) principal charge carriers are ions, (d) the electronic conductivity is negligible, (e) low activation energies for ion migration, and (f) special crystal structure with open tunnels or channels through which the mobile ions move [27,28-30].

II. CLASSIFICATION OF FAST ION CONDUCTORS

1. Crystalline/Polycrystalline Fast Ion Conductors

Crystalline fast ion conductors are characterized by the fast diffusion of one type of ion through the defect in the crystalline framework [31]. Broadly the defects are concentrated point defects or molten sublattice type defects. Mobile ions in most crystalline FICs are monovalent such as Li+ [32], Na+ [33], Cs+ [34], Cu+ [35], Ag+ [36], and F -[37] and sometimes it may be divalent such as O2- [38-40]. By the precise knowledge of the structure and the flexibility of the compositions, numerous crystalline solid electrolytes are synthesized. As a general rule, FICs have open crystal structure, which allows the rapid motion of ions. Thermal agitation is not necessary to create the defects in the ion conducting sublattice, since the sufficient number of empty sites are already available in the structure. lonic conduction in crystalline FICs is due to the motion of ions and or defect through the vacancies in the lattice [41]. Among the crystalline solid FICs, the highest conductivity is exhibited by silver ion conductors. Examples of crystalline superionic

materials and their conductivity are listed in Table 1. [42-54].

Apart from these a class of materials called NASICON (sodium superionic conductor) is significantly used as solid electrolytes due to their high ion conductivity and stability of their phosphate units. The crystal structure of NaA2IV(PO4)3 (AIV = Ge, Ti, and Zr) was investigated by x-ray in 1968 and became the first report related to NASICON family [55]. Another promising group of superionic conductors, LISICON (lithium superionic conductors) type have received much importance because of the high ion conductivity at room temperature. The LISICON compound Li14ZnGe4O16 and related systems (Li2+2xZn1-xGeO4) were first described by Bruce and West [56,57].

Table 1: Examples of Crystalline Superionic
Conductors with their Conductivities

Materials	Temp(K)	Conductivity(Scm-1)	
Silver ion conductors			
α -Ag ₃ I ₅	514	2.0	
RbAg ₄ I ₅	298	0.27	
α-AgI	420	1.0	
Lithium ion conductors			
Li_2SO_4	974	1.0	
Li ₄ SiO ₄	673	1.0×10^{-3}	
LiTa ₃ O ₈	723	1.5×10^{-2}	
Сор	per ion cond	uctors	
α-CuI	723	9.0×10^{-2}	
KCuI ₅	546	0.6	
Potas	sium ion cor	ductors	
Kβ-Alumina	573	6.5×10^{-5}	
Oxy	gen ion cond	luctors	
ZrO ₂ +Y2O ₃	1273	1.2×10^{-1}	
Bi2O ₃ +WO ₃	1023	1.0×10^{-1}	
Fluorine ion conductors			
β-PbF2	773	1.0	
CaF2	973	$4,0 \times 10^{-2}$	
Proton ion conductors			
Sb ₂ O ₅ :4H ₂ 0	$b_2O_5:4H_2O$ 298 3.0×10^{-4}		
Polytungstic acid	298	1.7×10^{-1}	

In addition to this, a new family of Li+ ion conductors with garnet type structure having general formula Li5La3M2O12 (M =Ta and Nb) was introduced by Thangadurai and Weppner [58]. It shows pure lithium ion conductivity and high

decomposition voltage (6V versus Li), making it suitable for application as an electrolyte in all solid state lithium ion secondary batteries [59].

2. Fast Ion Conducting Glasses

lonic conduction in glassy materials has been investigated since 1884, when Warburg placed a dc electrical field on a glass, and observed an electrolytic Na+ transport. Glass electrolytes characterized as amorphous structures are now widely used for solid state ionic devices such as lithium ion batteries, sensors, fuel cells, electrochromic displays [60]. This is mainly owing to their dense, homogeneous and flexible natures in comparison with crystals or ceramics.

Table 2: Silver Ion Conducting Glasses and the	ir
Conductivities	

No.	Silver Ion Conducting Glasses	Temperature (K)	Conductivit y(Scm-1)
1	AgI-Ag ₂ S-AgPO ₃	303	5.7×10^{-3}
2	60%AgI-23.3%Ag2O- 10%(0.8SeO ₂ +0. ₂ V2O ₅)	303	1.87×10^{-2}
3	50% AgI-25% Ag ₂ O- 25% P2O ₅	298	8.0×10^{-3}
4	66.67% AgI- 22.22% Ag ₂ O- 11.11%(0.3CrO ₃ +0.7 V ₂ O ₅)	303	1.01 × 10- ²
5	AgI-Ag ₂ O-SeO ₂ -V2O ₅	295- 323	2.61×10^{-2}
6	66.7% AgI-24% Ag ₂ O- 8.3% V ₂ O ₅	298	2.6×10^{-3}
7	58% AgI-19% Ag ₂ O- 23% WO ₃	298	3.1×10^{-2}
8	60%AgI-25.5%Ag ₂ O- 8.7%MoO ₃ - 5.8%As ₂ O ₅	298	1.65×10^{-2}
9	75%AgI- 25%Ag ₂ MoO ₄	298	1.4×10^{-2}
10	80%AgI-20%Ag ₂ CrO ₄	296	1.5×10^{-2}

The glassy materials have several advantages from a viewpoint of ion conduction in comparison with the crystalline such as: (i) a wide range selection of compositions, (ii) isotropic properties, (iii) no grain

boundaries, (iv)easy film formation, and (v) resistance to environmental effects. Ion conducting glasses of solid electrolytes demonstrate the electrical conductivity by means of motion of ions (anions or cations) in amorphous phase and exhibit generally much higher ionic conductivity than their crystalline counterparts [61]. The achievement of higher conductivities in glasses than the crystals was simply thought to be due to open structure with larger free space in the glass. Electrical conduction in ion conducting glasses is known to take place via hopping of mobile ions between available equivalent sites. Since, then, large numbers of superionic conducting glasses involve the variety of mobile ions viz Ag+, Li+, Cu+, Na+, F-, and O2- have been discovered [62]. Solid electrolyte AgI-AgPO3 has been used as a model of superionic conducting glasses and well-studied by various techniques such as neutron scattering, X-ray diffraction, and Raman scattering [63-66]. Some of the silver ion conducting glasses is summarised in Table 2.

3. Fast Ion Conducting Polymers

Polymers based fast ion conductors have received considerable attention because of their potential applications in solid state batteries and electrochromic devices [67-71]. The area of polymeric electrolyte materials have been developed remarkably after the discovery of the first ion conducting polymers in 1973, which was polyethene oxide (PEOs) complexed with an alkali metal salt by Wright et al [72-74], following that Armand and coworkers examined the ionic conductivity of PEO and polypropylene oxide salt complex and proposed their application as solid polymer electrolytes in high-energy density batteries [75,76]. Most of the emphasis on polymer FICs has been carried out on the improvement of the materials based polyethylene oxide and alkali metal oxide. The area of polymer electrolytes has passed through various stages in development. These promising materials can be classified into three categories, which cover solid polymer electrolytes, electrolytes, polymer-gel and polyelectrolytes. Solid polymer electrolytes are polymer salt complexes, which are obtained by dissolving a salt in the polymer matrix. Polymer-gel

electrolytes are prepared by incorporation of liquid electrolytes into polymer matrix. Polyelectrolytes are polymers which contain ionic centres as part of their constitutional repeating units. lonic conduction in polymer solid electrolytes (PSEs) takes place in the amorphous fraction of polymer matrix [69,77]. The crystalline structures in polymer electrolytes such as those with channels can be conducting amorphous more than their counterparts. The PSEs besides being mechanically flexible and corrosion resisted, have also some demerits like low ionic conductivity, high crystallinity and deteriorated mechanical stability. In order to overcome these defects and to improve the quality of properties, addition of inorganic inert fillers such as, TiO2, Al2O3, MgO, etc; to PSEs is found to be the effective route of getting rational combination of ionic conductivity and the mechanical stability [78-80]. Recent studies have shown that the size and shape of these fillers play important role in improving the properties of PSEs [81-83].

Table 3: Examples of Polymer Solid Electrolytes with
their Conductivities

Polymer	Temperature	Conductivity	
Materials	(K)	(Scm-1)	
PEO-Cul	303	10- ⁶	
(PEO) ₁₉ -Nal	298	10- ⁴	
(PEO) _{4.5} -	298	3 × 10- ⁷	
NaSCN			
(PEO)-KAgI₅	298	2 × 10- ³	
(PVA)-H ₃ PO ₄	298	10- ⁵	
(PEO)1000-	298	8.5 × 10- ⁶	
(NKSO ₂ Me) ₂			

4. Fast Ion Conducting Composites

Composite solid electrolytes of the ionic salt-oxide (MX-A) type can be considered a new class of superionic conductors with high ionic conductivity which occurs through via interfaces. The combination of high conductivity with the enhanced mechanical strength together with the wide prospects for the purposeful modification of the electrolyte properties by varying the type and concentration of the dopant makes these composites promising materials real for electrochemical system [84]. Composite materials

are heterogeneous materials of solid phases. The effect of heterogeneous doping strongly depends upon the chemical nature of the components and the morphology of the system. In some cases, only a weak increase in conductivity is observed; in the case when the adhesion energy between the components is high enough, much stronger effects can be observed, such as the stabilization of unusual metastable phases of ionic salt [85-88]. The elaboration of composites offers a new degree of freedom in the search for advanced functional materials, because specific properties can, to a certain degree, be tailored by mixing appropriate phases. In the domain of solid state ionics, two routes can lead to improved solid ionic conductors: a search for new compounds and structures sustaining high level of ionic conductivity and a modification compounds, of existing by heterogeneous homogenous or doping. Heterogeneous doping, on the contrary, involves mixing second phase with very limited solid solubility and formation of defect concentration profiles in the proximity of interfaces, the deviation from local electrical neutrality (space-charge) is the consequence of point defect equilibrium at

interfaces [89], apart from the improvement of the electrical properties, such as better shock resistance or higher strength. Although composite materials, in general, contain many different phases, literature in the field of solid state ionic deals primarily with two phase mixtures [90].

A new class of solid electrolytes interfaces called ion conducting electrolytes made up of ionic salt and insulating chemically inert component, affects the properties of composite materials at low and moderate temperatures [91].

In most cases, the second phase consists of nonconducting materials such as TiO2, Al2O3, which is nearly insoluble in the host material under the fabrication conditions [92,93]. The conductivity enhancement in composites can be explained in terms of the presence of a great number of surfaces and interfaces, which act as additional sources of point defect [94]. In 1973, Liang [95] observed an enhancement of confirmed for numerous ceramic composites, including dispersions of fine insulator particles in an ionic conductor, with a major contribution by J. B. Wagner [96] and his group. The majority of studies were made on monovalent cation conductors, such as lithium, silver, and copper halides, and the

Table 4: Examples of Composite Solid Electrolytes	
and their Conductivities	

Materials	Conductiv ity(Scm ⁻¹)	Temperat ure(C°)	Ref.
LiCl0 ₄ -Al ₂ O ₃	~ 10- ²	200	[85]
TII-50mTiO ₂	7.94 × 10- ⁷	127	[92]
TII-40mAl ₂ O ₃	3.16 × 10- ⁶	130	[93]
Lil-40mγAl ₂ O ₃	1.20 × 10- ⁵	25	[95]
$Lil-Li_2S-La_2O_2Sm$	3.00 × 10- ⁶	30	[97]
Li7La3Zr ₂ O ₁₂ -Li ₃ BO ₃	1.00 × 10- ⁴	30	[98]
$\label{eq:linear} \begin{split} \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}\text{-}\text{Al}_2\text{O}_3\\ \text{KNO}_3\text{-}50\text{mAl}_2\text{O}_3 \end{split}$	1.40 × 10- ⁴	30	[99]
KNO ₃ -50mAl ₂ O ₃	4.00 × 10- ⁴	200	[100]
(BaCl ₂) _{0.9} :(KCl) _{0.1} - 50mZrO ₂	1.0 × 10- ⁵	300	[101]
CsI-TiO ₂	~7.00 × 10- ²	480	[102]
$CsNO_3$ -60m γAl_2O_3	2.50 × 10- ⁶	253	[103]
0.9[0.75Agl:0.25Ag Cl]-0.1mTiO ₂	1.40 × 10- ³	30	[104]
0.85[0.75Agl:0.25Ag Cl]-0.1mCeO ₂	1.40 × 10- ²	30	[105]
Sbl ₃ -Ag ₂ SO ₄	2.10 × 10- ³	25	[106]
Cdl ₂ -50mAl ₂ O ₃	6.30 × 10- ⁷	157	[107]
NaSn ₂ F ₅ - 10mAl ₂ O ₃ (0.1 μ m)	1.73 × 10- ⁶	100	[108]

After this initial study, the conductivity enhancement in heterogenous materials was

including dispersions of fine insulator particles in an ionic conductor, with a major contribution by J. B. Wagner [96] and his group. The majority of studies were made on monovalent cation conductors, such as lithium, silver, and copper halides, and the lithium compounds, largest group being considering their importance in high energy density portable batteries. Besides Al2O3, other oxides, such as MgO, SiO2, CeO2, TiO2, and ferroelectric BaTiO3, were found to be effective second phases for ionic conductivity improvements. More recently, the composite effect was also observed in ceramic anion conductors, such as lead or calcium fluoride, or even in solids with trivalent cation conductivity, like aluminium and rare-earth wolframates. Examples of composite solid electrolytes are listed in Table 4 along with their conductivity values, where m stands for mole fraction.

III. MODELS FOR ION TRANSPORT IN GLASSES

The understanding of ion transport in glassy electrolytes appears to be even less developed than in crystalline conductors, which, is largely due to lack of the complete structural information related to ion transport. Different superionic conducting glasses exhibit different structural motifs and oversimplification of transport mechanism is difficult. Reviews on various transport models of superionic conducting glasses are available and some of the models are explained in this section.

1. Anderson and Stuart Model

Anderson and Stuart proposed that the carrier ion is intrinsically mobile and the activation energy is the sum of the energy required overcoming the electrostatic forces and strain component. They found the expression for two energies and predicted the activation energy for the diffusion of mobile ion in number of silicate glasses [109].

2. Random Site Model

In this model, all the ions of particular type are treated as potential carriers with a Gaussian distribution of activation energy. The ion mobility varies with distribution of activation energy and

thereby with glass composition. Generally, the variation of carrier concentration with glass composition is relatively small and hence, the conductivity variation with glass composition is controlled by change in ion mobility. This model successfully explained the conductivity dependence on composition in fluorite structured solid solutions [110].

3. Weak Electrolyte Model

Ravaine and Souquet [111] developed the weak electrolyte model. This has been applied to the conductivity studies of Na2O-SiO2 glassy systems. In this system, dissociated ions are assumed to occupy intersititial sites in the glassy network, while the associated ions are located at non-bridging sites. When alkali oxide is incorporated with silica, the bonds are broken. In these glasses, the ionic conductivity is found to vary considerably with alkali oxide contents. The variation of ionic conductivity with Na2O content was explained due to variation of concentration of mobile Na+ ions.

4. Diffusion Path Model

Diffusion path model depends on potentials traced by Ag+ ions with oxygen and iodide ions. The carrier concentration depends on the number of Ag+ ions which are located in the shallow potential and mobility depends on how long shallow wells are connected for a long period, they form a favourable path for ion transport. This type of path is called diffusion path and the model is called diffusion path model. In the glasses, diffusion path can be formed more easily, since the configuration freedom is maximum in the disordered system [112,113].

5. Diffusion Controlled Relaxation (DCR) Model

S. R. Elliott and B. B. Owens proposed the diffusion controlled relaxation (DCR) model for the microscopic transport mechanism of ions in glasses. According to this model, there are energetically stable sites for the mobile ions to reside in the oxide glassy structure. Ionic transport occurs by means of diffusive motion between the equivalent sites resulting in the primary relaxational event with a characteristic microscopic relaxation time. However, when a cation hops into one of the vicinal

equivalent sites will result in the creation of double occupancy known as interstitial effect on instantaneous relaxation process [114,115].

IV. THEORY OF IONIC CONDUCTION IN COMPOSITES

In composites, an attempt has been made to enhance the conductivity of a normal ionic conductor, MX (e.g., AgCl, Lil, etc.) by mixing it with an insulator (e.g., Al2O3 etc.) [116-119]. The conductivity of the complex (MX-A) is governed by ionic transport via the MX-A interface. It is determined by (i) conductivity of MX within the interface region, (ii) the effective thickness of the interface of the region, and (iii) the grain size and shape of the insulating particles. Four models are of interest:

1. Space Charge Layer Model

In case of the space charge layer model, the fundamental concept is that ions can be trapped at the interface core (this process is equivalent to a segregation phenomenon). The counter species, in general, a trapped ion vacancy, is then accumulated in the adjacent space charge regions. The driving force is the chemical affinity of a second phase towards the trapped ion. For example, basic oxides present many nucleophilic hydroxide surface groups, which can attract and fixcations. The space charge layer concept is a natural extention of volume defect thermodynamics, which takes the defect equilibrium at grain or phase boundaries into account [89,116,120].

2. Percolation Model

In this model, a network of randomly connected resistors involving the non- conducting particles is imagined. Conduction takes place by percolation of the electrolyte through the passage of random resistors. Percolation probabilities represent the likelihood that particles are clustered in ways that form connected conduction pathways, which is central to the effective functioning of a composite electrode [121,122]. The concept of coordination numbers is central to the practical implementation of percolation theory. Broadly speaking, the coordination number represents the number of

contacts a particular particle makes with its ions into intersititial sites and enhance the neighbouring particles [123].

The percolation micro-model has been validated through comparing with the simulated results by the random packing reconstruction method [124,125], which demonstrate the accuracy of the percolation micro-model in dealing with the composite electrode with poly-disperse particle size distributions.

3. Resistor Network Model

Dudney [126] made an attempt to enhance the conductivity in composite systems by considering random distribution of dispersoid in the matrix and the role of matrix dispersoid particle sizes and the interface. This model predicts a peak in the conductivity (σ) versus volume fraction of dispersed plot with the effect of grain size of the bulk and dispersed. The model also interprets the effect of thickness of double layer and mobility in the conductivity the dependence of maxima in σ versus volume fraction plot. This model is limited only to the case of Lil-Al2O3 composite solid electrolyte system [127].

4. Adsorption-desorption Model

A German scientist J. Maier [116,128] developed an effective quantitative tool for the treatment of redistribution of mobile species at a variety of interfaces and its consequences on ionic conduction parallel to the interfaces. He modified the space charge model by employing the principle of a parallel switching resistor. In this case, dispersoid acts not only as an inactive insulator, but also as a driving force for the evolution of a space charge region, which in turn causes enhancement in defect concentration at the interfacial boundary. With the dispersion of second phase into the matrix, metal ions will be attracted from or repelled into the matrix depending on chemical species present on the surface of dispersoid. In the case of attractive interaction, surface active dispersoids swipe away the cations from its regular sites and therefore, enhanced vacancy concentration (adsorption process), on the other hand in the case of repulsive interaction, the dispersoids drag metal

interstitial concentration (desorption process).

V. PREPARATION OF FAST ION CONDUCTORS

1. Solid State Reaction Method

The most widely used method for the preparation of superionic conductors is the direct reaction between solid reactants called solid state reaction. Though solid state reactions were known for a long time, it was only during the last few decades that interest has focused both experimentally and theoretically in revealing the secrets of the atomic structures of crystals and their reactivity. The general problem of solid state reaction is two-fold. Firstly, the experimental determination of reaction rate and morphology as a function of all independent variables and secondly, the calculation of the reaction rates and prediction of the morphology under a given set of independent variables in terms of the known thermodynamic and transport properties of the system under consideration. These require the knowledge of the atomistic mechanism of the fundamental steps such as nucleation, phase boundary, sintering, and diffusion. Such studies provide a valuable aid in the furtherance of the practical utilization of reactions in the solid state.

The advantage of the solid state reaction is the readily availability of precursors and low cost powder production for industrial applications [129]. This method is environment friendly and no toxic or unwanted waste is produced after its completion. For solid state reaction, in general some caution is necessary in choosing a suitable vessel material that should be chemically inert to reactants at high temperatures. Platinum, silica, stabilized zirconia and alumina containers are used for the synthesis of metal oxides, while graphite containers are employed for sulphide and others such as chalcogenides and pnictides. If one of the constituent is volatile or sensitive to atmosphere then reaction is carried out in sealed evacuated capsule.

2. Co-precipitation Method

In normal solid state reactions, the reactants are mixed together manually or mechanically and the subsequent reaction rate depends to a large degree on the particle size of the reactants, the degree of homogenization achieved on mixing and the intimacy of contact between the grains, as well as the obvious effect of temperature. By using coprecipitation procedures, it is sometimes possible to achieve a high degree of homogenization together with a small particle size and thereby speed up the reaction rate. This may be illustrated by the synthesis of ZnFe2O4 spinel. In one method, oxalates of zinc and iron are used as the reactants; these are dissolved in water in the ratio of 1:1, the solution then being mixed and heated to evaporate the water. Oxalates of zinc and iron are gradually precipitated together and the resulting fine powder is a solid solution that contains the cations mixed together essentially on an atomic scale. The precipitated solids are filtered off and heated in the usual way, but because of the high degree of homogenization, much lower reaction temperatures are sufficient for reaction to occur (e.g. ~ 1000 Co for the formation of ZnFe2O4). The overall reaction may be written as:

 $Fe2((COO)2)3 + Zn(COO)2 \rightarrow ZnFe2O4 + 4CO + 4CO2$

The method has also been successfully used for the preparation of other spinels such as; CoFe2O4, MnFe2O4 and NiFe2O4. The method does not work well in cases where (a) the two reactants have very different solubilities in water, (b) the reactants do not precipitate at the same rate or (c) supersaturated solutions commonly occur. Therefore, it is often not suitable for the preparation of high purity, accurately stoichiometric phases [130].

3. Vapour Phase Transport Method

An interesting and potentially valuable preparative method developed by Schafer (1971), is the method of chemical transport via the vapour phase. The method may be used for the synthesis of new compounds, for the growth of single crystals or for the purification of a compound. Basically, the

method consists of a tube, usually of silica glass, which contains the reactant(s) A, at one end and which is sealed, either under vacuum or more usually with an atmosphere of a gaseous transporting agent, B (Fig.2.a). The tube is placed inside a furnace such that a temperature gradient exists inside the tube; typically, there is a temperature change of 50 Co along the length of the tube. Materials A and B react together to form gaseous AB which subsequently decomposes at the other end of the tube to redeposit crystals of A (Fig.2.b).

glass tube

А	B (gas)	
	(a)	,
A	AB (gas)→	0 0 A00
T2		T1
	(b)	

Fig.2. Simple vapour phase transport experiment for the growth of single crystals of substance A.

The process shown in Fig.2. is for the simple case of transport of material A along the length of the tube. The method depends on the existence of a reversible equilibrium between reactant A, transporting agent B and gaseous product AB. If the formation of AB is endothermic, then, preferentially, the reaction to form AB occurs at temperature T2 (hot end) and gaseous AB is transported to the cooler end of the tube where it decomposes to deposit crystals of A at temperature T1. Conversely, if the formation of AB is exothermic, the reactant is arranged to be at the cold end of the tube and the product is formed at the hot end [131].

4. Ion Exchange Reaction Method

In structures which contain, for instance, an array that has open layers or interconnected channels, it may be possible to replace some of the cations by ion exchange and thereby synthesize new compounds. This has been done in the β - alumina family of compounds, because, they contain such suitable open channel type "conduction planes"

through which ion exchange is very much possible. fingerprint". An X-ray powder pattern is a set of By immersing lines or peaks, each of different intensity and

 β -alumina in suitable molten salts at for example, 300 Co, it is possible to exchange Na+ ion for a large variety of cations such as Li+, K+, Rb+, Ag+, Cu+, Tl+, NH4+, In+, Ga+, NO+, and H3O+. More recently, it has been found that divalent cations such as Ca2+ may enter the conduction planes by immersing in molten salts at 600 to 800 Co (to maintain electroneutrality, each Ca2+ replaces two Na+ ions). Ion exchange involves the equilibria of ions between crystal and melt and in particular, depends on the activities of the two cations involved in the crystal and melt.

VI. CHARACTERIZATION OF FAST ION CONDUCTORS

Once the superionic conductor is prepared, the next stage is to determine its structure, if this is not already known. For molecular materials, details of molecular geometry may be obtained from spectroscopic measurements. Alternatively, if the substance is crystalline, X-ray crystallography is used which gives information about molecular packing in a crystal. No single technique is capable of providing complete characterization of a solid. Rather, a variety of techniques are used in combination. Some of the techniques which are used frequently in the characterization of superionic solids are described here:

1. X-ray Powder Diffraction

X-ray powder diffraction (XRD) is one of the most powerful techniques for qualitative and quantitative analysis of crystalline compounds. When a material sample is irradiated with a parallel beam of monochromatic X-rays, the atomic lattice of the sample acts as a three dimensional diffraction grating, causing the X-ray beam to be diffracted to specific angles. The diffraction pattern, that includes position (angles) and intensity of the diffracted beam, provides some information about the sample. The angles are used to calculate the interplanar atomic spacings (d-spacing). Hence, every crystalline material will display a characteristic diffraction pattern and can act a unique,

fingerprint". An X-ray powder pattern is a set of lines or peaks, each of different intensity and position (d-spacing or Bragg angle, 2 θ), on either a strip of photographic film or on a length of chart paper (Fig.3). For a given substance, the line positions are essentially fixed and are characteristic of that substance. The intensity may vary somewhat from sample to sample, depending on the method of sample preparation and the instrumental conditions. For identification purposes, proper note is taken off line positions, together with a semiquantitative consideration of intensities.



Fig.3. Schematic X-ray powder diffraction pattern

Some of the applications of the of X-ray powder diffraction are:

Phase Identification

Each crystalline substance has its own characteristic powder diffraction pattern, which may be used for its identification. Standard patterns are given in the powder diffraction file known as the JCPDS, (Joint Committee on Powder Diffraction Standard) file.

Determination of Accurate Unit Cell Parameters

The position (d-spacing) of the lines in a powder pattern is governed by the values of the unit cell parameters (a, b, c, α , β , γ). Unit cell parameters are normally determined by single crystal methods but the values obtained are often accurate to only two or three significant figures.

Particle Size Measurement

X-ray powder diffraction may be used to measure the average crystal size in a powder sample provided the average diameter is less than 200 Ao using Debye-Scherrer formula based on width and intensity of the peaks.

Elucidate the Progress of a Solid State Reaction and Determines its Mechanism

The crystallinity of a solid state reaction mixture is temperature dependent, becomes crystalline on heating, which is verified by XRD pattern becoming sharper.

Crystal Defects and Disorder

Certain types of defects and disorder that occur in crystalline solids may be detected by a variety of diffraction effects.

2. Thermal Analysis

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of temperature. The production of new high- technological materials and the resulting requirement for a more precise characterization of these substances have increased the demand for thermal analysis techniques. Current areas of applications include environmental measurements, composition analysis, product reliability, stability, chemical reactions, and dynamic properties. An integrated, modern thermal analysis instrument can measure transition temperatures, weight losses, energies of transition, dimensional changes, modulus changes, and viscoelastic properties. Thermal analysis is useful in gualitative and quantitative analysis. Samples may be identified and characterized by qualitative investigations of their thermal behaviour. Information concerning the detailed structure and composition of different phases of given samples is obtained from the analysis of thermal data. Quantitative results are obtained from changes in weight and enthalpy as the sample is heated. The temperature of the phase change and reaction as well as the heat of the reaction is used to determine the purity of the materials. The use of microprocessors has both enhanced and simplified the techniques of thermal analysis. The multitasking capabilities of some computer systems allow a single microcomputer to operate several thermal analysers simultaneously and independently [132].

Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA)

Differential scanning calorimetry has become the most widely used thermal analysis technique. In this technique, the sample and the reference materials are subjected to a precisely programmed temperature change; when a thermal transition (a chemical or physical change that results in the emission or absorption of heat) occurs in the sample, thermal energy is added to either the sample or the reference containers in order to maintain both the sample and the reference at the same temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. Since DSC can measure directly the temperature and enthalpy of a transition or the heat of a reaction, it is often substituted by differential thermal analysis as a means of determining these quantities except in certain high temperature applications.

In DTA, the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature (usually the sample temperature). Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of differential ΔT, programmed temperature, versus the temperature, Τ, indicates the transition temperature(s) and whether the transition is exothermic of endothermic. DTA and thermogravimetric analysis (measurement of the change in weight as a function of temperature) are often run simultaneously on a single sample. DTA is very similar to DSC. A sample and inert reference are also used in DSC, but the cells are designed differently.

A useful rout is to follow the thermal changes on cooling as well as on heating. This enables separation of reversible changes, such as melting or solidification from irreversible changes as in most decomposition reactions. A schematic DTA sequence illustrating reversible and irreversible

change is shown in Fig.4.(a). Starting with a hydrated material, dehydration is the first event that occurs on heating and appears as an endotherm. The dehydrated material undergoes a polymorphic transition, which is also endothermic transition, at some higher temperature. Finally, the sample melts, giving the third endothermic transition. On cooling, the melt crystallizes, as shown by exothermic peak, and the polymorphic change also occurs, exothermically, on cooling, but, rehydration does not occur. The diagram shows two reversible and one irreversible process. It should be clear that if a particular process, on heating, is endothermic, then the reverse process, on cooling, must be exothermic.

On studying reversible processes, which are observed both on heating and cooling, it is common to observe hysteresis; for instance, the exotherm that appears on cooling may be displaced to occur at temperatures lower than the corresponding endotherm which appears on heating. Ideally, the two processes occur at the same temperature but hysteresis ranging from a few degrees to several hundred degrees is commonplace. The two reversible changes in Fig.4.(a) shown with small but definite hysteresis.

The universal applicability of DTA and DSC has led to their use in nearly every field of science, with strong emphasis on solving problems in materials technology and engineering as well in pure scientific investigations. The approach here is to divide the subject according to the basic features of a DSC/DTA curve; Fig.4.(b) shows most of the general features likely to be encountered. At the start of the heating, an offset, O, is usually apparent, which is due to an imbalance in the thermal capacities of the sample pan and its contents, and the reference pan and its contents. In the absence of any discrete physical or chemical transformations, the baseline signal, at B, is related to the heat capacity of the sample. DSC allows this parameter to be determined with good accuracy over a wide temperature range. The conventional approach is to compare the signals obtained for the sample above to that given by an empty pan, with the signal obtained for a standard material usually

sapphire, under the same conditions. A careful experimental technique is required to obtain accurate results, but heat capacities can be routinely measured to accuracies better than ±1%. The DSC/DTA curve may show a change, as at S in the curve, reflecting a change in heat capacity not accompanied by a discrete enthalpy change. The most common example, and a major application area of DSC, is the glass transition temperature (Tg) seen in amorphous polymers. This important region, in which the material changes from a rigid glassy state to a rubber, or very viscous liquid state, may be analysed to give a wealth of information about the material.

The DSC/DTA curve may show an exothermic or endothermic peak, as at EX and EN in the curve. The enthalpy changes associated with the events occurring are given by the area under the peaks. The peaks may be characterized by

- Position (i.e. start, end, extrapolated onset and peak temperature),
- Size (related to the amount of material and energy of the reaction),
- Shape (which can be related to the kinetics of the process).

Solid-solid reactions, such as those occurring in pyrotechnics as well as the decomposition characteristics of high explosives may be examined. The ability of DSC to use a small amount of samples is clearly of benefit here. Provided the heating rate and/or sample size is kept small enough, the rapid "runaway" reaction typical of these materials can be carried out in a controlled manner, and has been studied in detail.



Fig.4.(a) Schematic curves of reversible and irreversible changes.



Fig.4.(b) Schematic diagram of DSC/DTA curves

Thermogravimetric Analysis (TGA)

TGA measures the change in mass of a substance as a function of temperature or time. The sample is heated at constant rate until it begins to decompose. Under conditions of dynamic heating decomposition regularly takes place over a range of temperatures.

TGA may be used for various kinds of kinetic study. An accurate and rapid TGA method is used to study decomposition reactions isothermally; the TGA furnace is arranged at a pre-set temperature and the sample introduced directly at this temperature. After allowing 2 to 3 minutes for the sample to equilibrate at the furnace temperature, the decomposition of the sample with time can be followed. The process may be repeated at other temperatures and the results analysed to determine reaction mechanisms, activation energies, etc.

3. Fourier-transform Infrared (FT-IR) Spectroscopy

An infrared spectrum is articulated as a fingerprint of the sample with absorption peaks correspond to the frequencies of vibration between the bonds of atoms, which compose the material. Each material has unique combination of atoms; no two compounds generate the same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of materials. The main difficulty has arisen owing to slow scanning process. Hence, FT-IR spectroscopy was developed to overcome the limitations encountered with the dispersive instruments for measuring all of the infrared frequencies simultaneously rather than individually.

This employed a very simple optical device called an interferometer. The FT-IR spectrum of a sample is collected by passing a beam of infrared light (usually mid-IR; 4000-400 cm-1) through the sample. The size of the peak in the spectrum is a direct indication of amount of the material present. Thus, it is a very reliable technique for positive identification of almost any sample. The sensitivity benefits facilitate the identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it is batch to batch comparisons to quality standards or analysis of an unknown contaminant. Therefore, this technique is widely used to assure the composite, complex or solid solution formation.

4. Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) was pioneered by Manfred von Ardenne [133] and is a type of electron microscope capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. The SEM is a microscope that uses electrons rather than light to form an image. There are many advantages of using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be focussed at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. The preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most widely used instrument in research areas today [134-139].

5. Impedance Spectroscopy

Impedance spectroscopy (IS) has been extensively used in various fields such as aqueous corrosion, battery testing and in the developments of electrolytes for solid oxide fuel cells (SOFCs). It is an electrochemical technique where the response is analysed from electrodes and electrolytes upon a

small-amplitude alternating voltage, which is varied Where ϵo is the permittivity of the free space (8.854) over a wide frequency range at various potentials and determination of all the electrical characteristics of interface, which can be thought as a thin capacitor that forms between the charged electrode and counter ions lined up parallel to it [140]. Either one of the electrodes or the electrolytes can be the sample.

Two or four electrodes are used in the setup and the electrolyte can be solid, aqueous or a film. Impedance spectroscopy is able to determine a number of parameters related to electrochemical kinetics and polarizability, for instance, the polarization resistance of corroding electrodes in an aqueous electrolyte, the state of charge for batteries and the effect of microstructure on the conductivity of the solid electrolytes [141].

Impedance is a more general concept than resistance because it takes phase differences into account and becomes a fundamental and essential concept in electrical engineering. Impedance spectroscopy provides a simple technique to deduce various contributions of the total conductivity of electrical materials in terms of four possible complex formalisms, viz., impedance (Z^*) , admittance (Y*), modulus (M*) and permittivity (ϵ *). These parameters are interrelated as follows:

$$Z^* = (Y^*)^{-1}$$
 (1)

$$Y^* = J\omega_o s^*$$
(2)

$$s^* = (M^*)^{-1}$$
 (3)

$$M^* = J\omega C_o Z^* \tag{4}$$

Where, ω is angular frequencies ($\omega = 2\pi f$) and Co is the vacuum capacitance of the measuring cell and electrodes having air gap in place of sample and defined as:

$$C_o = s_o(\frac{A}{l}) \tag{5}$$

 \times 10-14) and A and I are cross sectional area and thickness of the pelletized sample respectively.

To analyse the experimental impedance spectra, data usually are modelled by an ideal equivalent circuit consisting of a resistor (R) and a capacitor (C) [142,143]. Most of the superionic conductors possess two semicircles (one at high frequency and another at low frequency region) with or without spike as shown in Fig.5.

The high and low frequency semicircles assigned respectively to the grain and grain boundary contributions to the total electrolyte impedance, while the contribution of electrode- electrolyte interface to the impedance (also produce doublelayer capacitance, Cdl) is clearly represented by inclined spike appearing at very low frequencies [144,145]. The circuit for each semicircle in this case consists of a parallel combination of R and C unit.

The complex impedance plane plot appears in the form of a series of semicircles attributed to the relaxation phenomena with different time constants due to the contribution of grain, grain boundary and electrode in a polycrystalline material.

It is guite remarkable to note the resistance of grain boundary may not necessarily be larger than the grain. It may be due to the fact that the grain boundary layer is of several magnitudes thinner than the grain.

Hence, the contribution to overall electrical property by various components in the material is separated out easily. The total AC conductivity of the sample is given by:

$$\sigma = \frac{1}{Rt} \times \frac{l}{A}$$

Where A is flat surface area and I is thickness of the pellet used.



Fig.5. Complex AC impedance plane plot.

6. Ionic Conductivity

Electrical conduction occurs by the long range migration of either electrons or ions. Usually conduction by one or other type of charge carrier predominates, but in some inorganic materials both ionic and electronic conduction are appreciable in the same material. In solid materials, one is usually interested in the specific conductivity, σ , which is the conductivity of a crystal of pellet that has a cell constant of unity, i.e., unit cross-sectional area and unit length. Commonly used units of specific conductivity are ohm-1cm-1, ohm-1m-1, and Sm-1 where 1 siemen, S = 10hm-1.

For any material and charge carrier, the specific conductivity is given by

$$\sigma = \Sigma i ni ei \mu i$$

where ni is the number of charge carriers of species i.e., is their charge and μ i their mobility. For electrons and monovalent ions, e is the charge on an electron, 1.6 × 10-19

C. Conductivities are usually temperature dependent and for all materials, except metals, the conductivities increases with increasing temperature. In metals, σ is highest at low temperatures and in some metals the phenomenon of superconductivity occurs close to absolute zero. Migration of ions does not occur to any appreciable extent in most ionic and covalent solids such as oxides and halides. Rather, the atoms tend to be essentially fixed on their lattice sites and can only

move via crystal defects. Only at high temperatures, where the defect concentrations become quite large and the atoms have a lot of thermal energy, does the conductivity become appreciable, e.g., the conductivity of NaCl at ~ 800 oC, just below its melting point, is ~ 10-3 S cm-1, whereas at room temperature, pure NaCl is an insulator with the conductivity much less than 10-12 S cm-1 [146].

In contrast, there exists a small group of solids called, solid electrolytes, fast ion conductors and superionic conductors, in which one of the sets of ions can move quite easily. Such materials often have rather special crystal structures in that there are open tunnels or layers via which the mobile ions may move. The conductivity values, e.g., 10-3 ohm-1 cm-1 for Na+ ion migration in β -alumina at 25 oC, are comparable to those observed for strong liquid electrolytes. There is currently great interest in studying the properties of solid electrolytes, developing new ones and extending their range of applications in solid state electrochemical devices.

VII. APPLICATION OF FAST ION CONDUCTORS

1. Sensor Technologies

Oxygen sensors have received immense importance in various applications for determining oxygen contents of gases and liquids. Typically, they are fabricated from the tube of an oxide ion conductor such as yttria stabilized zirconia (YSZ), bismuth oxide (in oxidizing environments) or thoria (in reducing environments). Sensor technologies can be used to detect ammonia (NH3), one of the useful gases extensively used in several chemical industries, refrigeration systems as well as fertilizer factories. Though, ammonia gas is very toxic and their exposure at higher concentration is hazardous to mankind. In order to prevent the serious accidents caused by NH3 gas leakage, development of smart gas sensing tools, which can precisely measure NH3 gas concentration at every emitting site is greatly expected [147].

2. Solid State Batteries

Li-ion batteries represent one of the popular types of rechargeable batteries for portable electronic

devices like laptop computers, mobile phones, digital cameras and electronic vehicles [148]. Li-ion batteries offer high energy and power densities, slow loss of charge when not in use, abundant and relatively low cost, and they do not suffer from memory effects [149,150]. Because of many of their benefits, including their high energy density, Li-ion batteries have also been increasingly in aerospace, back-up storage, and transportation applications.

3. Electro-chromic Devices

An electro-chromic device is made up of conductive materials and electrolyte, which allow the color changes when an electric field is applied to cause a reversible redox reaction [151]. They can be commonly used in architectural smart windows [152] as well as indoor comfort for buildings [153]. And thereby, reduces the energy expenditure even on a national level [154]. Electro-chromic materials have received considerable attention due to their potential applications such as information displays, windows, aircraft windows, smart variablereflectance mirrors, eyeglasses, skylights, sunroofs 5. David A. Keen, J. Phys. Cond. Matter.14 (2002) and variable thermal radiators [155].

4. Solid Oxide Fuel Cells

Solid oxide fuel cell (SOFC) is the most efficient technology for the conversion of chemical energy of fuels such as hydrogen and hydrocarbons directly into electrical power [156]. SOFCs also operate in reverse mode to produce hydrogen and oxygen (steam electrolysis) or syngas from CO2 and steam (co-electrolysis) [157,158]. The SOFC traditionally operates between the temperatures 900-1000 oC. However, lowering the operation temperature of SOFCs to an intermediate range 600-800 oC, not only significantly improves the material compatibility for the SOFCs, but, also reduces the production costs of SOFC systems [159].

VIII. CONCLUSION

The typical characteristic of the fast ion conductors is that the lattice possesses enormous amount of vacancies through which the movement of ions can take place. In such systems, opportunities of different kinds of ordering exist and, moreover, the

ordering is reflected in ionic conductivity. Fast ion conductors clearly pose some of the most challenging problems in the study of atomic transport mechanisms in solids. There has been remarkable progress in the last decade, especially in the study of fluorite structured materials and a class of materials called NASICON (sodium superionic conductor), which have been widely used as solid electrolytes due to their high ion conductivity.

REFERENCES

- 1. Rafiuddin, M. Hassan, Solid State Commun.144 (2007) 293-295.
- 2. H. Lee, N. Park, Curr.Appl.Phys.13 (2013) 1444-1447.
- 3. Mohammad Hassan, Ahmad Noman Al-hakimi, Rafiuddin, Arabian Journal of Chemistry 4 (2011) 45-49.
- A.R. West, 2003. Solid State Chemistry and Its 4. Applications. Wily, Singapore, pp.453.
- R819-R857.
- 6. M. Prudenziati, J. Hormadaly, Materials Science and Applications in Sensors, Electronics and Photonics Elesevier (2012).
- 7. Gerald D. Mahan and Walter L. Roth, Superionic Conductors (2013).
- Armin Bunde, Klaus Flunke, Malcolm D. Ingram, 8. Solid State Ionics 105 (1998) 1-13.
- 9. M. Faraday, Expermental Investigation in Electricity (Quarritch, London (1839).
- 10. M. Faraday, Philos. Trans. R.Soc. Richard and J. Taylor, London (1838).
- 11. W. Hittrof, Ann. Phys. Chem. 84 (1851) 1.
- 12. E. Warburg, Ann. Phys. Chem. N. F. 21 (1994) 662.
- 13. E. Warburg and F. Tegetmeier, Ann. Phys. Chem. N. F. 32 (1888) 455.
- 14. M. Katayama, Z. Phys. Chem. 61 (1908) 566.
- 15. W. Nernst, Z. Electrochem. 6 (1900) 41.