CHAPTER-I

Introduction to Oxygen Ion Conductor

An expert is a person who has made all the mistakes that can be made in a very narrow field.

Niels Bohr

1.1 Introduction

Solid compounds which exhibit high ionic conductivity are termed as solid electrolytes or superionic conductors or fast ion conductors. The mobile anions or cations present in the electrolyte which can move freely throughout the crystalline structure are responsible for the conduction process. Solid electrolytes are intermediate in between metals and insulators and, their conductivities lie in the range 10^{-5} - 10^{-1} S/cm, the magnitude of which is same as that of semiconductors and aqueous electrolyte materials [1]. Extensive investigation are being conducted on solid electrolytes in recent years as these materials offer a wide range of potential technological applications, such as high energy-density batteries, fuel cells, sensors etc. Solid electrolytes provide important advantages over liquid electrolyte in many ways which include the elimination of sealing problems, minimal undesirable chemical, thermal and acoustic emissions and particularly miniaturize the size so that it can be suitably used in compact devices.

1.2 Solid electrolytes and their classification .

The solid electrolytes are disordered ionic materials which exhibit high ionic conductivity comparable with those of liquid electrolytes and molten salts. These materials are characterised by: (a) high electrical conductivity (between 10^{-2} and 10^{-1} ohm^{-1}.cm^{-1}), (b) ions as the principal charge carriers with negligible electronic conductivity, (c) small barrier to migration of ions (activation energy less than about 1 eV), (d) a very unusual and open crystal structure with tunnels or layers through which the ion can migrate in the electric field [2-3]. There exist a large number of crystalline materials with low ionic conductivity due to the fact that the ions or atoms in them can vibrate about their mean (atomic) positions. However, in case of solid electrolyte it posses freely moving cations or anions which can move freely from one crystal lattice site to another crystal lattice site. Therefore, solid electrolyte can be placed as intermediate between normal crystalline solids having no mobile ions or atoms but with a regular array and liquid electrolyte which have no regular structure but mobile ions.

Most of the solid electrolytes yield efficient applications only at high temperature. At comparatively low temperatures, they exhibit a common type of crystal structure and undergo a phase transition which has low ionic conductivity. With the increase of temperature the defect concentration increases and the ions vibrate more vigorously. As a result the ionic conductivity increases at higher temperatures. Based on the structure and phases, solid electrolytes can be broadly classified into the following categories:

    a) Crystalline and polycrystalline
    b) Glasses
    c) Polymers
    d) Composites

1.2.1 Crystalline and polycrystalline solid electrolytes

These types of solid electrolytes possess one type of ions with high mobility which can diffuse through the defects that exist in the crystal structure. Depending on the species of the mobile ions responsible for the conduction process, it can be further classified as cationic, anionic and protonic conductors. Transport mechanism in crystalline and polycrystalline materials is originated from the thermally activated hopping of ions between the crystal lattice sites. A large number of crystalline solid electrolyte materials of different cations and anions such as H^+, Na^+, K^+, Li^+, F^-, O^{2-} etc. were extensively studied and reported **[4-7]**.These materials have the special crystal structure providing tunnels or channels giving pathways for ions to migrate. Among them α-AgI, MAg_4I_5 (M = Rb, K) **[7-11]** and Na β-alumina **[12-13]** display remarkably higher ionic conductivities. In the recent times a large number of investigations have been carried out on lithium ion conductors because of the smaller ionic radius of Li^+, modest weight and its prospective use in high energy density batteries [**14-16**].

On the other hand, oxygen ion conductors are a very interesting subgroup of this type of solid electrolyte which displays high anionic conductivity where the oxide ions (O^{2-}) are the charge carriers. Oxygen ion conductors have been widely investigated for use as components of fuel cells, oxygen sensors, oxygen pumps and oxygen permeable membrane catalysts **[3, 17-19].**

1.2.2 Glass electrolytes

As compared to the crystalline electrolyte, glass electrolytes have some advantages such as nonappearance of grain boundary, isotopic conduction, easy fabrication of films into different shapes and so on. They are described as amorphous structure. Due to the dense homogeneous and flexible nature, glass electrolytes are found to have wide applications in lithium ion batteries [20], fuel cells [21-22], and electrochromic displays etc [23]. In 1970, silver ion conduction was discovered in oxyhalide glasses and was called as fast ion conducting glass or vitreous solid electrolyte [24]. Later, a large number of silver ion conducting glass electrolytes were reported. At the same time extensive investigations have been carried out on lithium ion conducting glasses as solid electrolyte for solid state lithium ion batteries [25-27].Since then, various researchers have successfully reported a large number of works on glass electrolyte compounds with various ionic species, like Ag+, Cu+, Li+, Na+ , H+ , F⁻ etc. [28].

1.2.3 Polymer electrolyte

The structure of polymer electrolytes is a combination of both crystalline as well as amorphous phases. But high ionic conductivity is mainly found in the amorphous phases [29-30]. Detailed study on these substances reveals that the transport phenomena in polymer electrolyte are due to the continuous motion of the ions in the amorphous region of the electrolyte and not as a consequence of hopping of ions from site to site [31-32]. The liquid-like conductivity exhibited by this type of solid electrolyte without the movement of the solvent itself was found interesting and promising as it can be easily fabricated into complex shapes (not possible in the case of liquid electrolyte) and safer than liquid electrolyte. Considerable attentions have been paid on this type of electrolyte due to its potential applications in solid state batteries and various electrochromic devices. For such applications, Polyethylene oxide (PEO) is considered as the most suitable polymer electrolyte [33]. However, from the practical standpoint of view it cannot be regarded as ideal electrolyte because the room temperature conductivities of PEO based electrolytes are found to be in the range of 10^{-6}-10^{-8} S/cm [34-35]. Addition of inorganic filler to the polymer electrolyte has increased the electrical conductivity and mechanical properties [34-35].

1.2.4 Composite electrolyte

The composite electrolytes are multi-phase materials containing two or more solid phases and exhibit enhanced mechanical, thermal and electrical properties **[36]**. The composite electrolytes usually show higher ionic conductivity. The overall conductivity of the electrolyte is remarkably higher than in both the constituted phases. The ionic conductivity observed in the electrolyte is supposed to be originated from the high ionic conductivity in the interface between the components **[37-38].** The improved conducting behaviour of composite electrolyte was reported for the first time on Li:Al$_2$O$_3$ composite system **[39]**. Since then, a large number of investigations have been conducted on various composite systems such as insulator-conductor or conductor-conductor system **[37-40,]**. The ceria-based dual phase electrolyte is a novel category of composite electrolyte which plays an important role in the development of functional electrolyte for low temperature solid oxide fuel cell **[41-43].** Much attention has been paid on ceria-based composite system by incorporating different salts and hydroxides. The ceria-based composite system shows a high ionic conductivity of 10^{-2}-10^{-1} S/cm in the temperature range 400 to 660 ^{o}C and also possesses a good fuel cell performance **[41-43]**.

Since, the present work is related with the structural and electrical properties of oxygen ion conductor, more details about the electrical properties of oxygen ion conducting ceramics are discussed below.

1.3 Solid oxygen ion conducting electrolyte

A very interesting subgroup of solid electrolytes is the materials that display oxygen ion conductivity, known as oxide ion conductors, where the oxide ions are the charge carriers. An oxide ion conducting electrolyte, in general, conducts only O^{2-} ions and in real sense it behaves as an electronic insulator under operating conditions. Oxide ion conductivity is a specific property of some solids that was discovered more than a century ago by Nernst in Zirconia derivatives **[3, 17-18, 44-46].** In oxygen ion conductor current flow is due to the movement of oxide ions inside the crystal as a result of thermally activated hopping mechanism**.** For a conductor to be good ionic conductor it requires that the crystals must contain unoccupied sites equivalent to those occupied by the lattice oxygen ions. Moreover, it should also be stable in both

oxidizing and reducing condition during the cell operation. The primary requirement for oxygen ion conductor is that it must possess high oxygen ion conductivity and negligible electronic conductivity. It is not easy to achieve this situation because owing to the high mobility of electrons and holes in comparison to ionic carriers can generate considerable electronic contribution even for the low concentration of electronic carriers [3]. Hence most of the oxygen ion conductors are in real sense mixed conductors and only a few can be classified as pure ionic conductors.

Although several oxygen ion conducting electrolyte materials for SOFC have been developed in recent years, they are not free from problems regarding technological as well as commercial point of view. For example, some materials display higher ionic conductivity but they are expensive and hence offer big disadvantage for extensive applications. In the field of oxide ion conductor, ZrO_2, CeO_2 and Bi_2O_3 based solid electrolytes are considered as the most suitable electrolyte materials for solid oxide fuel cell [47-50]. Among them, conductivities of the compounds derived from Bi_2O_3 are found to be higher in comparison to the others [51-53]. The various oxide ion conducting solid electrolytes developed by different groups of researchers are discussed below.

1.3.1 Zirconia-based oxide ion conductors

The most widely investigated and well known solid electrolytes for SOFCs are the materials based on zirconia or ceria [54-57]. As already pointed out, YSZ is the most commonly used solid electrolyte, which possesses ionic conductivity around 0.1 S cm^{-1} at 1000 °C for solid solutions with 8 mol% yttria [54]. Pure ZrO_2 exhibits a very low ionic conductivity due to the absence of sufficient interstitial oxide ions and vacancies. However, on substitution of Y (yttrium) with the general formula $Zr_{1-x}Y_xO_{2-\delta}$ for Zr, introduces vacancies giving rise to high oxygen ionic conductivity. These materials possess higher ionic conductivity and good stability in both oxidizing and reducing atmosphere as well as negligible electronic conductivity. To stabilize high temperature tetragonal cubic structure and to generate oxide ion vacancies in zirconia based materials, lower valance dopants are introduced in the cation sub lattice [54].

Scandium-doped zirconia also emerges as a promising electrolyte due to its better ionic conductivity, but with limitations regarding the cost of Sc and long-term stability. Another work on Co-doping with yttrium stabilizes the cubic structure and avoids the poor thermal cycling stability [58]. Calcia-doped zirconia is an advantageous electrolyte regarding the cost of material. But the problem with such electrolyte is that its ionic conductivity is less than the desired value and also reduced performance due to significant ohmic losses. The operating temperature of stabilized zirconia is ~ 1000 °C. Various problems like high cost of materials, stability, compatibility and thermal degradation of the materials etc. are associated with high operating temperature which limits their applications. Therefore, continuous attempts have been made to fabricate new electrolyte systems that possess higher ionic conductivity at relatively lower temperatures.

1.3.2 Ceria-based oxide ion conductors

Ceria-based electrolytes systems are imperative due to their much better ionic conductivities than zirconia based materials. The prime limitations with such materials include the low redox stability which is accompanied by increasing electronic conduction and chemical expansions [54]. These effects are less prominent at low temperatures and hence these electrolytes are found prospective applications for low or intermediate temperatures [59-62]. The best dopants in ceria-based electrolytes are Gd and Sm. The highest conductivities are generally found in the substitution range 10–20 at% which is of the order of 10^{-1} S cm^{-1} at 800°C (same as for YSZ at 1000°C) [60]. However, for higher substitution level, the defect interaction strongly increases [63-65].

1.3.3 Bi$_2$O$_3$-based oxide ion conductor

Electrolyte materials derived from bismuth oxide exhibit superior ionic conductivity in comparison to other solid electrolyte [66-69]. Pure bismuth oxide possess two thermodynamically stable structural polymorphs: α- polymorphs (stable below 730°C) and δ-polymorph (stable above 730°C up to the melting point) [70]. The maximum ionic conductivity is obtained for stabilized δ-Bi$_2$O$_3$ with highly oxygen deficient fluorite structure. Since α- Bi$_2$O$_3$ is a very low conducting oxide phase, a large number of attempts including doping by rare earth have been made to stabilize the

high conducting δ-Bi_2O_3 phase [71]. Unfortunately, bismuth oxide based materials posses a large number of constraints which restrict their practical applications. Some of the major problems can be sorted out as, sensitivity towards reduction, tendency to volatilization, low mechanical strength etc. However, the performance of these materials is far better than the best ceria-based materials as the ionic conductivity of doped Bi_2O_3 is above 10^{-1} S cm^{-1} at temperatures as low as 650°C [71-72].

1.3.4 LaGaO$_3$-based oxide ion conductors

Of the perovskites till investigated, LaGaO$_3$-based electrolyte systems are the most interesting system which exhibit ionic conductivities higher than YSZ and thus become promising materials for SOFC applications in intermediate range of temperature [3]. The system is generally known as LSGM, where Sr and La are doped at Mg and Ga site respectively. Both these dopants are found to generate oxide ion vacancies due to their lower valence state and hence lead to a higher ionic conductivity. The highest conductivity reported for this compound is of the order of 0.14 S cm^{-1} at 800°C [73-75]. It is difficult to obtain phase pure LSGM, as small loss of Ga oxide is usually associated with sintering at high temperatures. Therefore, some small impurity phases are generally present in the compounds; however, the impact on the overall conductivity is accounted insignificant [76]. Further investigations reveal that addition of small amount of dopant such as Co, Fe improve the performance without introduction of electronic conductivity [77-78].

### 1.3.5 La$_2$Mo$_2$O$_9$-based (LAMOX) oxide ion conductors

Another interesting group of oxide ion conductor, called LAMOX family, was developed by Lacorre [79] in Le Mans. The parent compound of these materials is $La_2Mo_2O_9$ which possesses ionic conductivity comparable to those of the other existing electrolytes at temperatures above 600°C [3, 80]. At this temperature, the compound undergoes a $\alpha \rightarrow \beta$ type of phase transition and exhibits a remarkable increase of ionic conductivity, approximately two orders of magnitude, associated with this phase transition. The high temperature β-$La_2Mo_2O_9$ having a cubic lattice is isostructural with β-$SnWO_4$ [81-82]. Incorporation of Bi^{3+} into La^{3+} and rare earth cations (Gd, Dy, Y) and/or substitution of V^{5+} or W^{6+} in the Mo-site were able to suppress the $\alpha \leftrightarrow \beta$ phase transition [83]. The major disadvantages with LAMOX

family are: relatively high electronic contribution, tendency towards reduction and reactivity with the electrodes **[84-85]**. To overcome these difficulties, major improvement of this material is needed for practical applications in different electrochemical devices.

1.3.6 $Bi_4V_2O_{11}$-based (BIMEVOX) oxide ion conductors

BIMEVOX compounds derived from the parent compound $Bi_4V_2O_{11}$ by partial substitution for vanadium with a metal are considered as the best oxide ion conductors at moderate range of temperatures (400 to 600 $^{\circ}$C). $Bi_4V_2O_{11}$ is structurally perovskite-related type built up from $(Bi_2O_2)^{2+}$ layers separated by $[VO_{3.5}\square_{0.5}]$, perovskite like slabs, where $\square$ stands for oxygen ion vacancy. **Fig. 1.2** shows the ideal structure of the γ-phase, which is often called a single-layer aurivillius structure **[86]**.
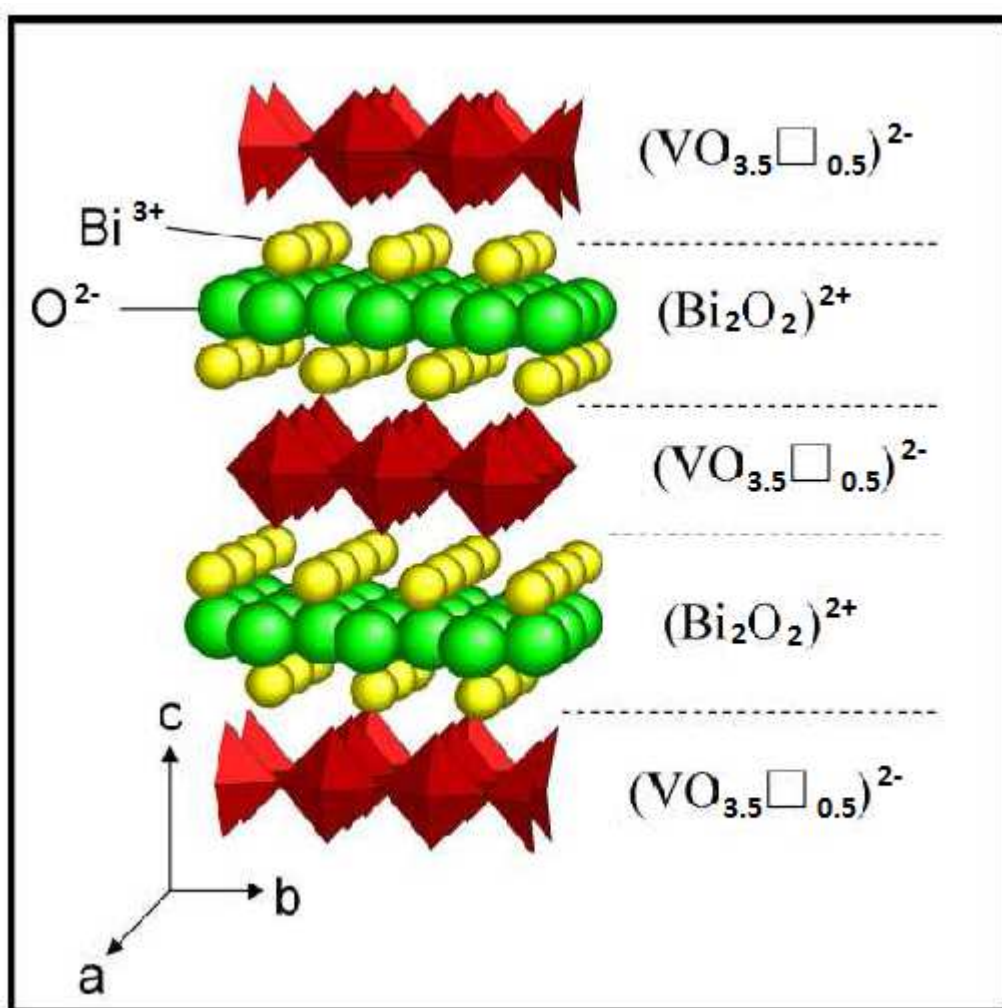
Fig. 1.1: Ideal structure of γ-phase consisting alternating Bi-O and V-O layers [**86**].

Upon heating, it shows three principal polymorphs. The α-polymorph is stable between room temperature to 430 °C, the β-polymorph between 430 °C and 570 °C while highly conducting γ-phase is stable at high temperatures, between 570 °C to 870 °C which is also the melting point of the material [87]. The high conducting γ-$Bi_4V_2O_{11}$ phase possesses good ionic conductivity due to presence of vacancies in the perovskite vanadate layers sandwiched between bismuth layers [88]. Ionic transport occurs essentially via oxygen anion hopping between these oxygen vacancies. The high temperature γ-phase can effectively be stabilized down to room temperature by partial substitution of V-sites by aliovalent meal ions like Cu, Co, Ti, Ni, Nb, Zr etc. [87,89-91] resulting in enhanced oxide ionic conductivity at intermediate temperature. A wide range of metals can be substituted into the V-site and most of them found to stabilize the high temperature γ-phase at relatively low temperature [89].

Among the dopants studied, Sb, Cu and Ti appeared to yield the best oxide ionic conducting properties with conductivity as high as ~10^{-2} S/cm at 320 °C for Sb doped materials [90]. A maximum conductivity of the order of ~10^{-3} S/cm was observed for $Bi_4Cu_{0.2}V_{1.8}O_{11-\delta}$ at 300 °C which becomes a good candidate as solid electrolyte in intermediate temperature SOFC operation [87]. For Ti doped BIMEVOX the highest ionic conductivity is observed in $Bi_4V_{1.7}Ti_{0.30}O_{10.70}$ with σ = 4×10^{-4} S cm^{-1} at 230 °C [89]. Similarly, in case of Ni substituted BIMEVOX low temperature conductivity appears to be about 1.7×10^{-3} S cm^{-1} at 300 °C which is lower than the maximum value of 2.1×10^{-3} S cm^{-1} obtained BICOVOX for the same dopant concentration [91].

Substitution of V by Mo or W appeared to stabilize only the β-polymorph [92]. With Uranium (U), the γ-polymorph could be obtained depending on dopant concentration [93]. Studies on monovalent dopant such as Li and Na did not lead to improvement in oxide ion conductivity. It has been reported that rare earth doped (Nd, Gd, Er, Yb etc) bismuth vanadate exhibits conductivity values 2×10^{-4} S/cm at 300 °C [94]. Although, these materials appear to be β-polymorph, their conductivity values are close to those reported for γ-phases of certain compounds such as when La, Fe and Nb are introduced as dopants. Similarly, when doped with Cd, it is reported that highest conductivity of ~1.3×10^{-4} S/cm at 420 °C was observed [92].

The degree of ionic conductivity depends on the metal selected for doping as well as on the level of substitution. There is wide range of scope for working with bismuth

vanadate based material. It is learnt from the literature that substitution on V as well as Bi-site is possible. A large number of works has been reported on V-site substitution. On the other hand, only scanty reports are there on Bi-site substitution **[95-96]** and still there is a lot of scope for the studies to be carried out on the effect of substitutions at Bi-site on the ionic conductivity of BIMEVOX.

1.4 Various structures of oxygen ion conductors

Ionic conductors are characterized by rapid diffusion of ion species through the crystal lattice. Extensive interests have been focused on oxygen ion conductors to develop new electrolyte system having high oxygen mobility at moderate temperatures (400-800 $^\circ$C). As high oxygen ion mobility is related to the lattice vacancy, there are two methods to increase ionic conductivity- by discovering new oxygen ion conducting materials with intrinsic lattice vacancies or to introduce lattice vacancies in the known oxygen ion conducting materials extrinsically, i.e., by substitution of another metal to the compound by the process of doping so that extrinsic vacant sites are created in the crystal lattice. On the other hand, there should be small barrier for migration of mobile species. It seems to be difficult to obtain the required small barrier because of the fact that the ionic radius of oxygen ion which is the largest component of the lattice is higher (1.4 Å) than the metal ions. Therefore the crystal structure of the compounds should be favorable for oxygen ions to migrate. Fortunately, there exist certain materials having very unusual and open crystal structure and are the oxygen ion conductors. These materials having highly disordered open crystal structures can be classified into different categories which are discussed below.

1.4.1 Fluorite structure

The fluorite-structured oxides are the traditional oxide ion conducting materials which were derived from the early investigations of Walter Nernst. The basic structure for a fluorite structure can be described as face centered cubic packing of cations, with anions in all of the tetrahedral holes as shown in **Fig. 1.3**. The crystal structure of fluorite can also be viewed as a simple cubic array of oxygen lattice with eight coordinated cations in the centre of alternate cubes. The general crystal structure describes the materials of the type AO_2, where A is a large tetravalent cation. The

readily available forms of fluorite structure are UO_2, ThO_2, CeO_2 and ZrO_2 **[97-98]**. The Zr^{4+} possesses fluorite structure either at high temperature or upon substitution by other cations. High temperature δ-Bi_2O_3 also exhibits fluorite structure. The oxygen vacancies generated by the process of doping provide the equivalent sites allowing oxygen ions to migrate. The metal ion such as Zr^{4+}, however, has twice the charge of an O^{2-} ion, and thus every vacancy cannot be filled with a Zr^{4+} without violating electro neutrality. Accordingly, only half of the vacancies are occupied by a Zr^{4+} ion, which results in intrinsic vacancy creation. A special characteristic of fluoride structure is that it is stable over a high degree of substitution which makes it as highly disordered materials **[3]**.
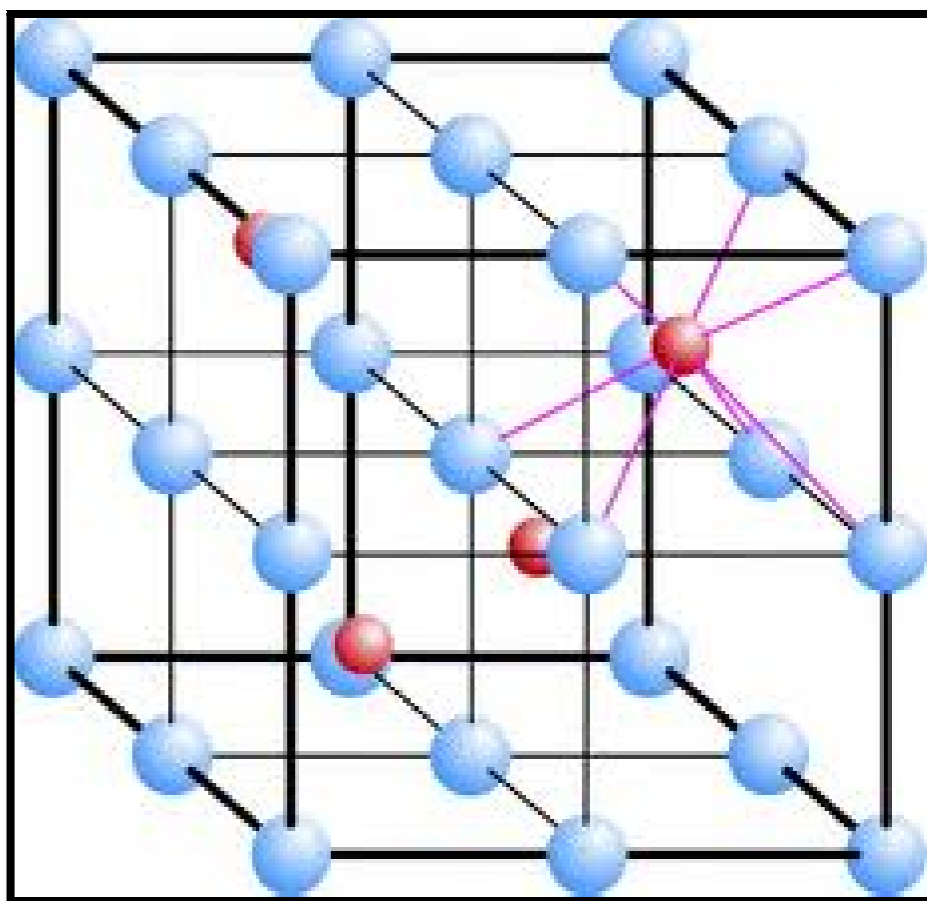
Fig.1.2: The fluorite (AO_2) structure (red spheres represent A cation and blue sphere oxygen ions) [**3**].

1.4.2 Pyrochlore structure

The pyrochlore structure is derived from an oxygen deficient fluorite structure. The structure denoted by the general formula $A_2B_2O_7$ is shown in **Fig.1.4**. The crystal

structure of pyrochlore compounds is generally regarded as a cation-ordered fluorite derivative with 1/2 vacant oxygen site per fluorite formula unit [83]. The unoccupied sites act as the channels or pathways through which the oxygen ions can migrate. Furthermore, the structure $A_2B_2O_7$ is capable of generating anion vacancies by doping in both the sub-lattices (A and B-site). In spite of these favouring factors, pyrochlore structured compounds possess poor conducting behaviour compared to the fluorite-type compounds [83]. The highest values of oxygen ion diffusivity in pyrochlore-type compounds have been reported for $Gd_{2-x}Ca_xTi_2O_{7-\delta}$ with $x \approx 0.2$ [83]. These materials also show a significant electronic conductivity under oxidizing and strongly reducing conditions.
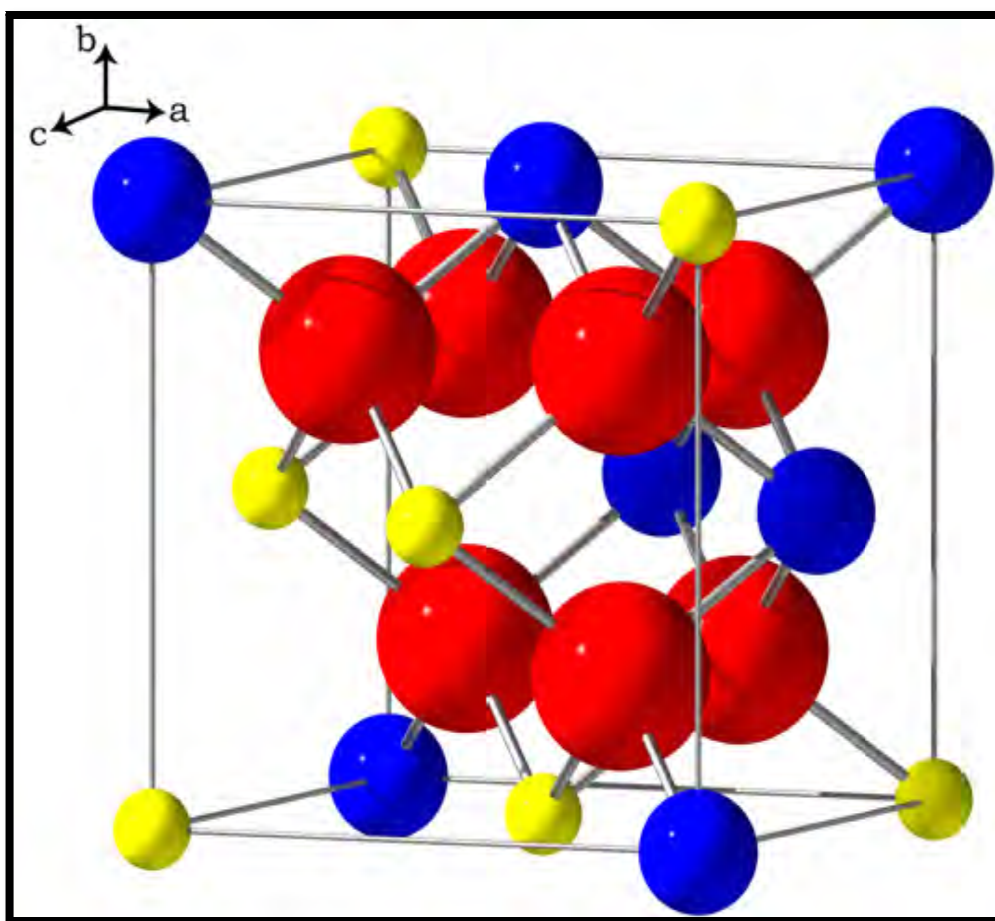
Fig.1.3: Pyrochlore oxide structure. The small spheres (yellow and dark blue) represent cation sites and the large spheres (red) represent the oxygen ions [99].

However, in most of the pyrochlore compounds, the electronic contribution also cannot be further improved by doping due to the restriction on solubility limit of variable-valence cations.

1.4.3 Perovskite structure

The structure of the materials of the type ABO_3, where 'A' and 'B' are metal cations, is denoted as perovskite structure. As shown in **Fig. 1.5**, the simplest way to represent perovskite structure is a cubic unit cell with 'A' cation at the corners, oxygen atoms at the midpoints of the edges, and a 'B' cation in the center. Perovskites were first discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist L.A Perovskite [100]. Generally, the 'A' site cation is large (such as rare earth) and has 12-fold coordination with anions. The 'B' site cation is usually smaller and normally a transition metal with 6-coordinated anions forming BO_6 octahedra. Most of perovskite structures are distorted and do not have cubic symmetry. Perovskite materials are very attractive because higher vacancy generated via lower valence cation doping on both the cation sub lattices, leading to higher ionic conductivity. A large number of perovskite oxides are purely oxygen ion conductors
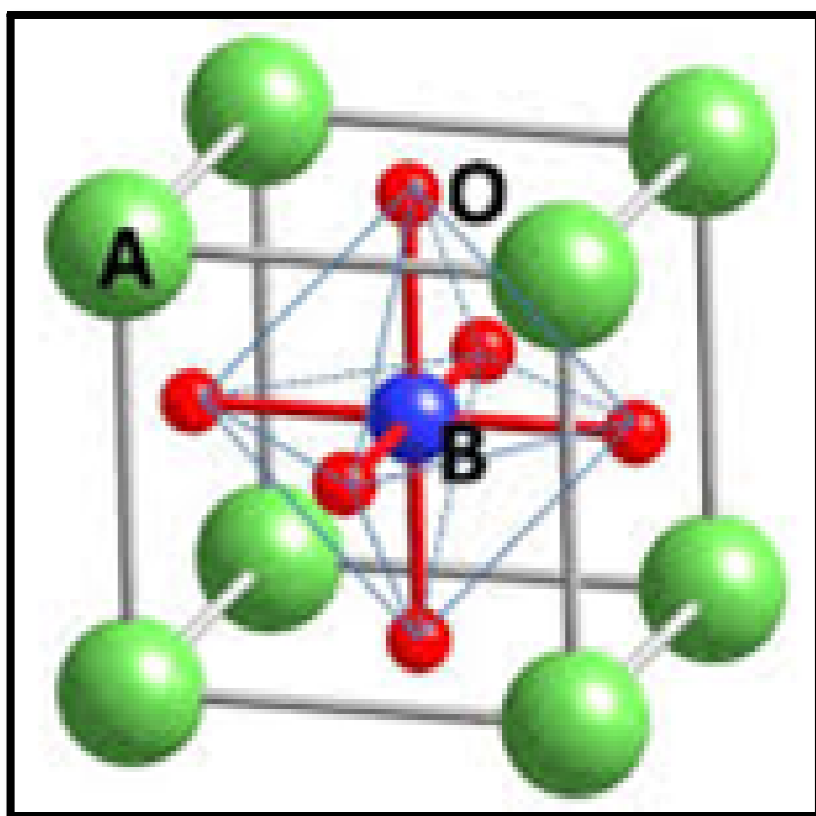

Fig.1.4: Perovskite ABO_3 structure with 'A' cation (green sphere), 'B' cations (blue sphere) and oxygen atoms (red sphere) [100].

and are promising materials for electrochemical cell operating in intermediate temperature range (600-800 ^oC) [83]. Among the numerous perovskites, only the

compounds based on lanthanum gallate ($LaGaO_3$) are found suitable for ionic applications. The ionic conductivity of doped lanthanum gallate with general formula $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM) exhibits the higher ionic conductivity comparable to fluorite type materials in the intermediate temperature [3]. The shortcomings of LaGaO3-based electrolytes are accounted as the possible reduction and volatilization of gallium oxide, the relatively high cost of gallium and significant reactivity with different cell components [83].

1.4.4 Brownmillerite structure

The Brownmillerite structure, as shown in **Fig.1.6,** is of the type $A_2B_2O_5$ where 'A' and 'B' are cation sites. It is named after the chemist Lorrin Thomas Brownmiller, Alpha Portland Cement Company, Easton, Pennsylvania, who identified for the first time in naturally occurring minerals. It is derived from perovskite structure with increased number of vacancies in ordered state which are disordered in perovskite structure [102]. This type of transformation has been accounted for quite a lot of perovskite type oxides of the series LaSrCoFeO for lower Fe content.
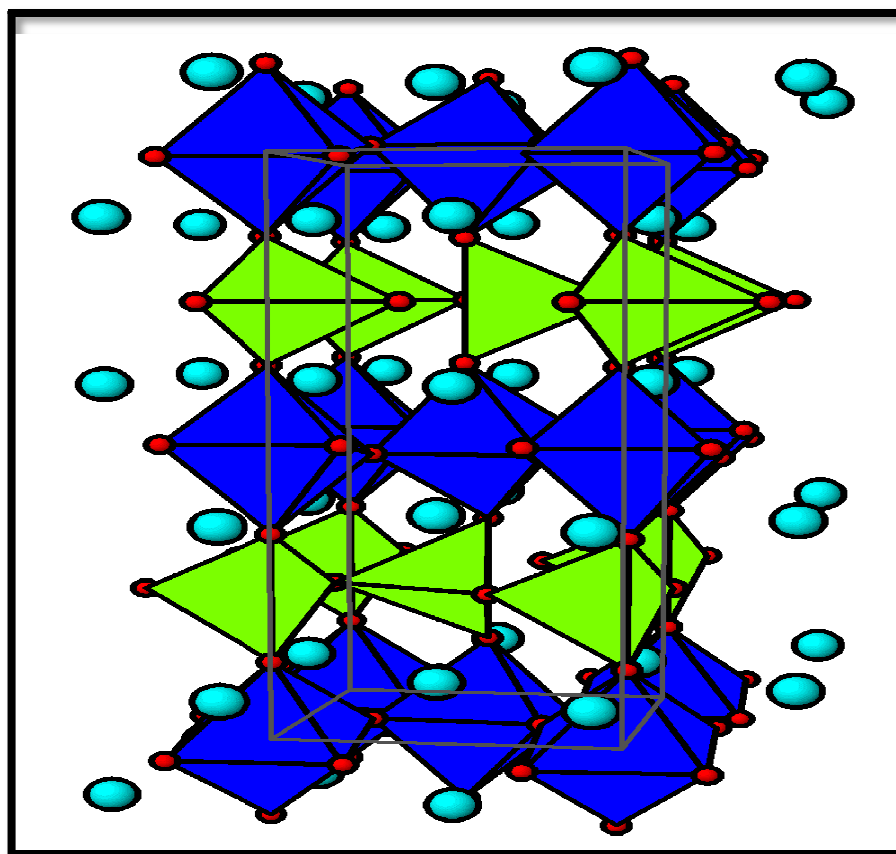
Fig 1.5: Brownmillerite structure [**103**].

The Brownmillerite structure formed by intergrown with perovskites possesses oxygen ion vacancies without aliovalent substitution. The Brownmillerite compound like $Ba_2In_2O_5$ shows mixed conductivity with dominant ionic transport. Doping with higher valence cations in barium sub lattice stabilizes the disordered cubic perovskite structure leading to the raise of ionic conductivity in the intermediate range of temperature [83].

1.4.5 Aurivillius structure

Aurivillius Structure, first reported by Aurivillius in 1949, consists of infinite 2D slabs of perovskite (ABO_3) type structure which are separated by other pattern [104]. But the oxide ion conductivity of this structure was first investigated by Takahashi [51] and Yanovski [105] in 1970. The structure of aurivillius structured bismuth vanadate ($Bi_4V_2O_{11}$) is shown in **Fig.1.7**.

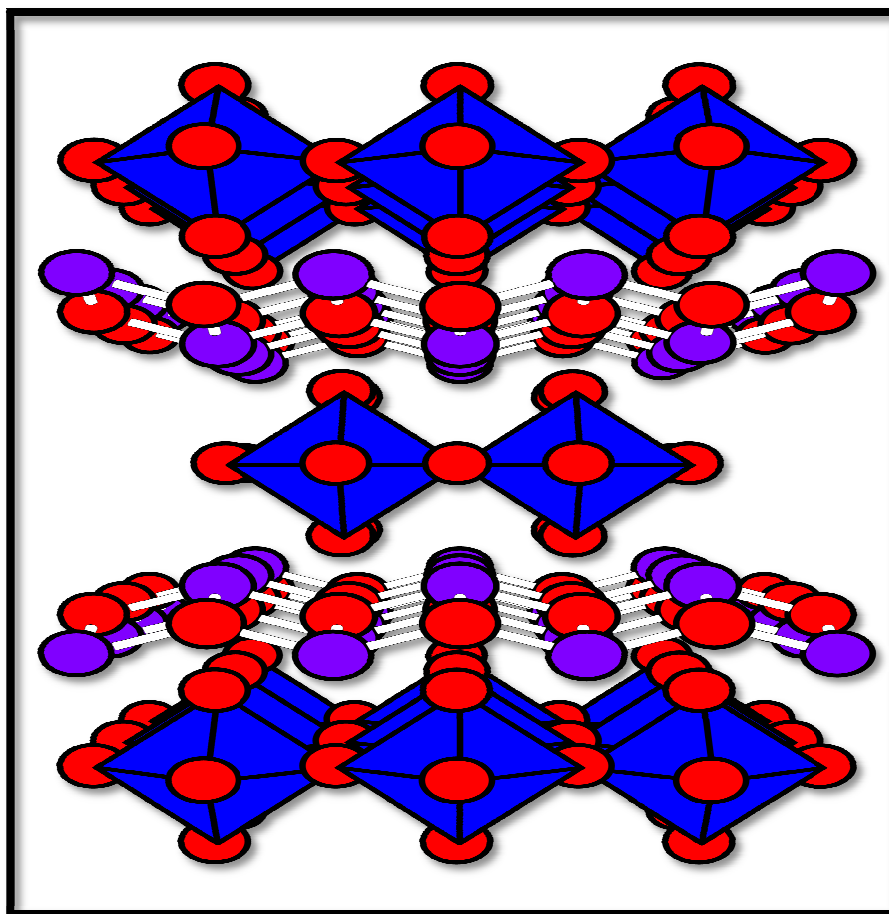**Fig.1.6:** Aurivillius structure of $Bi_4V_2O_{11}$ [103].

The distinguishing characteristics of this structure are (1) the special pattern which separates the layers, and (2) the offsetting of the layers from each other. The oxygen ion vacancies present in the perovskite layer give rise to a higher ionic conductivity, as reported in the systems Bi_2WO_6 and $Bi_4V_2O_{11}$ [106]. The structure of these materials consist of alternating layers of $(Bi_2O_3)^{2+}$ separated by perovskite slabs $(A_{n-1}B_nO_{(3n+1)})^{2-}$. The A and B-sites can accommodate a large variety of cations such that both the layers mentioned above must match structurally.

Among the various aurivillius oxides investigated till date, the family of $Bi_4V_2O_{11}$ (BIMEVOX) emerges as the most outstanding one due to their high ionic conductivity at relatively low temperature [107].
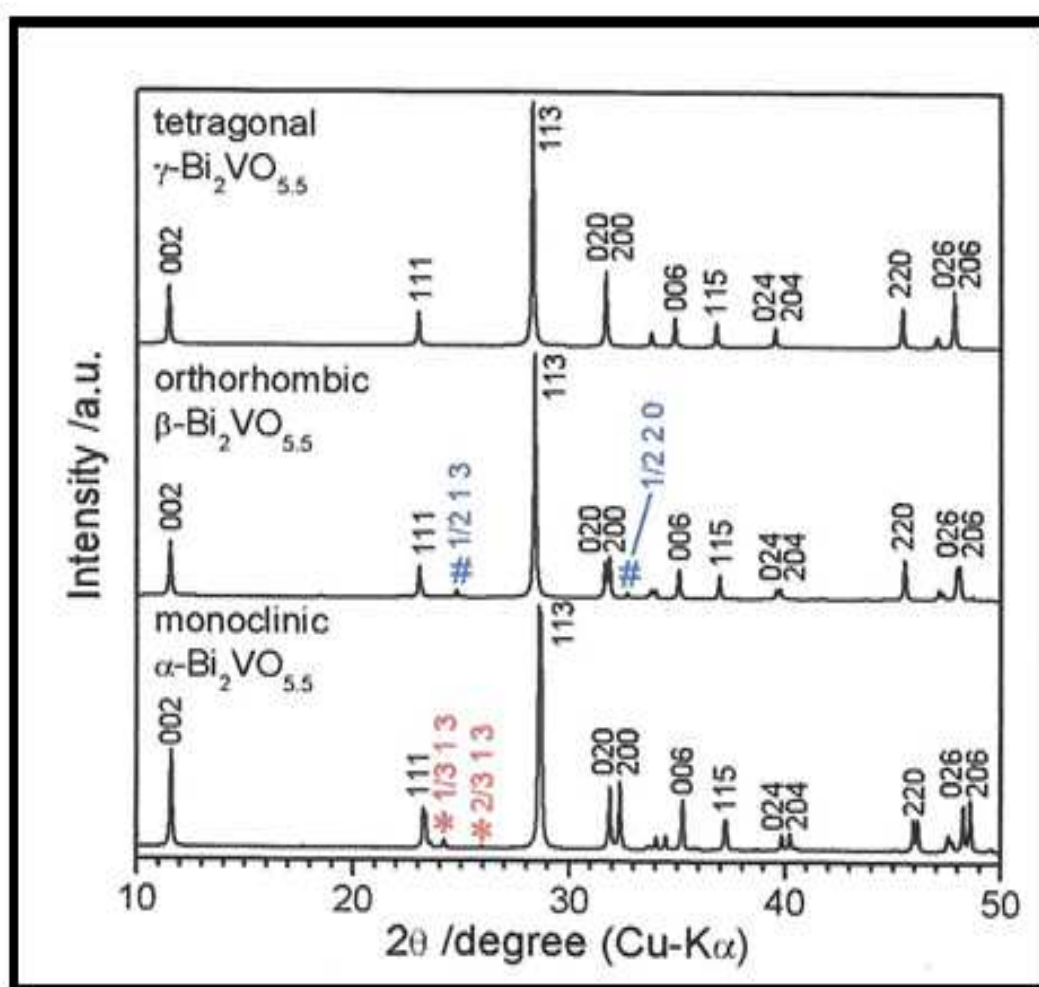
Fig. 1.7: Calculated XRD patterns for α, β and γ- $Bi_4V_2O_{11}$. The asterisks (*) and hash marks (#) indicate the typical superlattice diffraction peaks of α and β-$Bi_4V_2O_{11}$, respectively [86].

The crystallographic relationship of the three different polymorphs have been characterized with respect to a mean orthorhombic cell of dimensions $a_m \approx 5.53$, $b_m \approx 5.61$, and $c_m \approx 15.28$ Å [108-111]. The α-phase is a monoclinic cell of $a \approx 3a_m$, $b \approx b_m$, and $c \approx c_m$, the β-phase is an orthorhombic cell of $a \approx 2a_m$, $b \approx b_m$, and $c \approx c_m$, and the γ-phase is a tetragonal cell of $a = b \approx a_m/\sqrt{2}$ and $c \approx c_m$. **Fig. 1.8** shows the XRD patterns of the parent compound $Bi_4V_2O_{11}$ calculated from Cu-K$_\alpha$ radiation. The diffraction peaks are indexed on the orthorhombic sub cell of a_m, b_m, and c_m. All the three main phases exhibit similar sketches except for split peaks such as 2 2 0 at about 46° and characteristic superlattice diffraction peaks (*e.g.*, 1/3 1 3 at about 24° for α-phase, 2/3 1 3 at about 26° for the β-phase). On the other hand, no superlattice diffraction peaks are observed in the γ-phase and some diffraction peaks such as 0 2 0 and 2 0 0 at about 32° are merged to a singlet.

1.5 Principle of formation of defects

Ionic conduction in solid materials usually occurs by the long range diffusion of one or more species of ions from one site to another through the defects present within the crystal lattice. Therefore, solid electrolytes must possess freely moving cations (e.g. H^+, Na^+, Li^+, Ag^+) or anions (e.g. O^{2-}, F^-) together with vacancies along which the ions can move throughout the crystalline structure. In an ideal crystal the ions are arranged in a regular pattern and there is little space for diffusion of ions. However, at any non-zero temperature the regular patterns are interrupted by crystallographic defects. Solid electrolytes usually have freely moving cations or anions that move throughout the crystalline structure.

The lattice defect essential for ionic conduction in crystals is the point defect which includes 'Schottky' and 'Frenkel' defect [112-113]. Such type of defect is essential for hopping of ions within the crystal lattice. If in an ionic crystal an equal number of cations and anions are missing from their normal lattice site so that the overall electrical neutrality and stoichiometry is maintained, the crystal imperfection is said to be Schottky defect **[Fig.1.8 (a)]**.
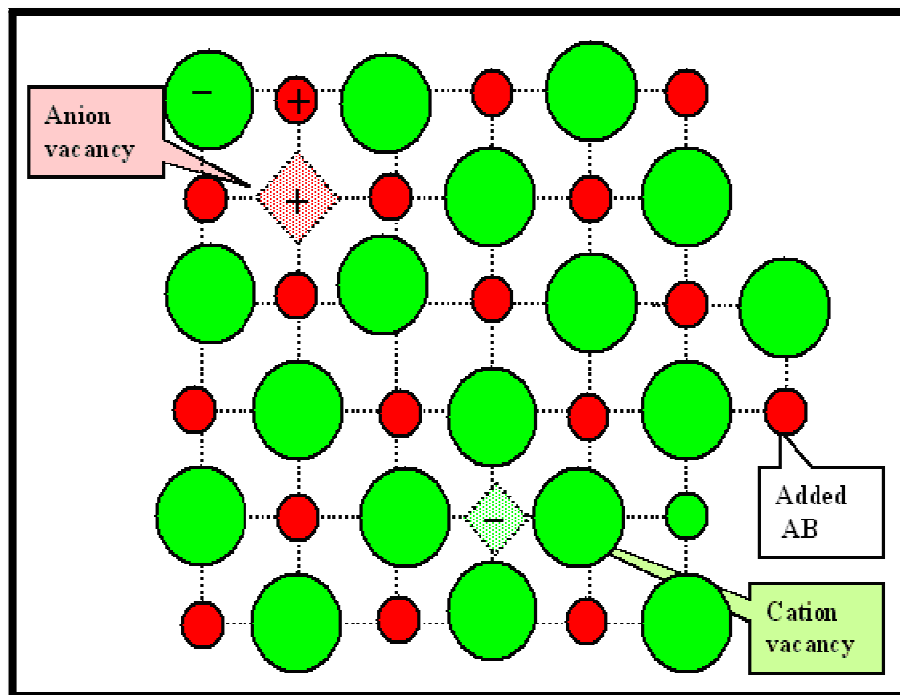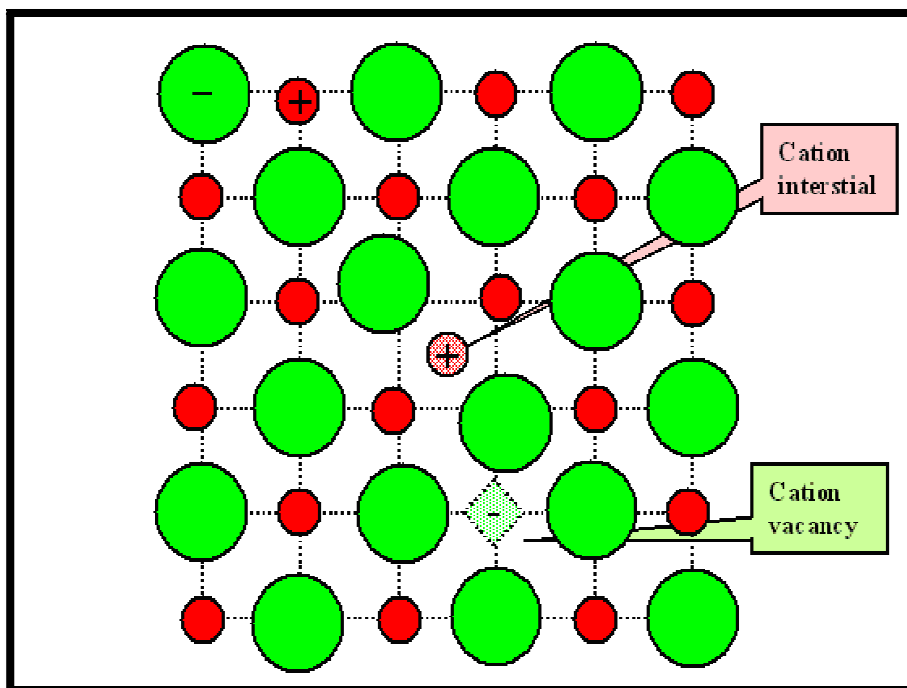
Fig. 1.8(a): Schottky Defect.

Fig. 1.8(b): Frenkel Defect.

On the other hand, when a single ion disappears from its normal position and occupies interstitial site in a nearby location which is not usually occupied by an ion, it is called a Frenkel defect **[Fig. 1.8 (b)].** These defects may be intrinsic or extrinsic. Intrinsic

defect is accompanied by thermal disorder and the extrinsic defect is the result of addition of aliovalent impurity. In a crystal, both the Frenkel and Schottky defects create vacant sites. Any neighbouring atom located near the vacancies can make a jump to one of the vacant sites leaving the previous site of the ion vacant which could again accommodate another ion. In this way ions make movements from one site to other site and as a result give rise to ionic conductivity.

The probability (P) of occurrence of a particular vacant site is proportional to the Boltzmann factor. In equilibrium,

$$P = exp\left(-E_v/k_B T\right) \tag{1.1}$$

Where E_v is the amount of energy required to create a vacancy, i.e., the energy required to transfer an atom or ion from lattice site to surface. If there are N atoms, the equilibrium number of vacancies n is given by the Boltzmann factor,

$$\frac{n}{N-n} = \exp\left(-E_v/k_B T\right) \tag{1.2}$$

If $N \gg n$, then it can be written as,

$$\frac{n}{N} = \exp\left(-E_v/k_B T\right) \tag{1.3}$$

The equilibrium concentration of vacancies decreases with the decrease of temperature. The formation of vacancy pairs keeps the crystal electrostatically neutral. With the help of a statistical calculation, it can be shown that **[113],**

$$n \cong N \exp\left(-E_p/2k_B T\right) \tag{1.4}$$

Where E_p is the energy required to form a pair. Similarly, for placement in an interstitial, it can be expressed as,

$$n \cong N\, N' \exp\left(-E_I/2k_B T\right) \tag{1.5}$$

Where N' is the number of interstitials and E_I is the energy required to remove an atom from its lattice site to an interstitial.

1.6 Diffusion and ionic conduction in solid electrolyte

Diffusion is the process of particle movement driven by a concentration gradient [114]. Ionic conduction arises from the activated hopping through the defects present in the crystal (vacancy, interstitial). Fick's first law relates the particle flux J_p to the gradient of concentration N of these particles,

$$J_p = -D.\nabla N \tag{1.6}$$

Where D is the diffusion coefficient.

The temperature dependence of the diffusion constant D can be expressed empirically by the Arrhenius relation [113-114],

$$D = D_o \exp\left(-E_a/k_B T\right) \tag{1.7}$$

Where E_a is the activation energy for the mass transport, D_0 is the pre exponential factor, k_B is the Boltzmann constant and T is the temperature.

The Nernst–Einstein expression relates the ionic conductivity to the diffusion coefficient of ions and suggest that the conductivity [115],

$$\sigma = nq^2 D \Big/ k_B T \tag{1.8}$$

Where n is the number of ions per unit volume and q is its charge.

1.7 Application of solid electrolyte

In the recent years, solid electrolytes are widely used as large and small power sources, electrochromic devices like smart windows and many other devices [116]. As the requirements for cheap and clean electrical energy source increasing, fuel cells appear to be one of the most efficient and effective solutions to environmental problems that we face today. The uses of solid electrolytes in various devices with special emphasis on solid oxide fuel cell are summarized below.

1.7.1 Solid electrolyte cell

Much attention have been paid on solid electrolyte due to their prospective use as solid electrolyte battery in diverge field. The liquid electrolyte conventionally used in batteries suffers from the problem of limited durability due to the corrosion reaction between electrolyte and the electrode. Moreover the problem of leakage is always associated with liquid electrolyte. Solid electrolytes have the advantages such as, extremely low emission of pollutants, having no problem of electrolyte management, expectation of long life, operative over a wide range of temperature, miniaturization etc. The aqueous electrolyte cannot be used as power source in electronic circuit board whereas the solid electrolyte batteries can serve the purpose as they can be miniaturized and free from the problems of leakage. Some other types of room temperature operated batteries which are used in electronic watches, heart pacemaker etc.

1.7.2 Oxygen sensors

Oxygen sensor is a device which is employed to monitor the oxygen content and emission pollutants like NO_2 and CO_2 in an internal combustion process in modern electronic fuel injection system. In fact, it finds out the level of air-fuel ratio in a combustion engine so as to maximize the power output and hence the efficiency. Oxygen sensor itself cannot measure the air or the fuel entering the engine. But, if the information obtained from the sensor is coupled with the information from other sources, it can determine the air-fuel ratio. Moreover, efficient combustion process controls the emission level which can reduce the amounts of unburnt fuel as well as polluting oxides entering the atmosphere. Generally, the oxygen sensors used in various devices are fabricated from yttria-stabilised zirconia (YSZ), bismuth oxide (in oxidising environments) or thoria (in reducing environments) **[117]**. The YSZ based sensor is presently used in many devices whose operating temperature is above 800 ^{o}C. Ongoing researches have been conducted to develop advantageous sensors with desirable lower operating temperature (200-400 ^{o}C) **[118]**.

1.7.3 Oxygen pump

The principle used in oxygen pump is same with the principle of oxygen sensor. To work as oxygen pump the two electrodes of the cell are short-circuited and oxygen gas may then be pumped from one electrode compartment to the other [117]. The devices based on the above principle are commercially available in the form of oxygen purifier or to offer controlled oxygen atmospheres in studies of the corrosion of metals and the cultivation of micro-organisms etc [117].

1.7.4 Solid electrolyte thermometer

Solid state thermometer is used to measure high temperatures. As the material used in solid electrolyte thermometer is ceramic, it has the advantage of working at an elevated temperature i.e. higher than 1000 $^\circ$C.

1.8 Fuel cell

Fuel cells are electrochemical energy conversion devices which directly convert chemical energy of the fuel into electricity and heat through electrochemical reactions. Electrochemically a fuel cell is similar to a conventional battery with the difference that in a fuel cell the fuel is supplied externally whereas a battery uses internal fuels to generate electricity. Fuel cell can produce electricity as long as the fuel is supplied where as a battery has to be recharged once the internal fuel is used up. Fuel cells are becoming a promising source of alternate energy for future generation due to its higher efficiency of energy conversion and zero or near zero emissions [119]. As there is no combustion in a fuel cell, it can convert the fuel more efficiently into electricity than any other electricity generating sources available today. The various types of fuel cells with their characteristic features, application, advantages and disadvantages are tabulated in **Table-1.1.**

The different types of fuel cells are distinguished by the kinds of electrolyte they used and their corresponding operating temperature. The different types of fuel cell differ from each other regarding the kind of chemical reactions that take place in the cell, the types of catalysts used, the range of temperature in which the cell works, the fuel required, and other features. Moreover, these factors determine the suitable

applicability of the cell in various devices. There are several types of fuel cells, each with its own advantages, limitations, and potential applications.

Table-1.1: characteristics and comparison different types of fuel cells [**120**].

Fuel Cell Type	Polymer Electrolyte Membrane (PEM)	Alkaline (AFC)	Phosphoric Acid (PAFC)	Molten Carbonate (MCFC	Solid Oxide (SOFC)
Common Electrolyte	Solid organic polymer polyperfluorosul fo-nic acid	Aqueous solution of potassium hydroxide soaked in a matrix	Liquid phosphoric acid soaked in a matrix	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	Solid zirconium oxide to which a small amount of yttira is added
Operating Temperature	50 - 100°C	90 - 100°C	150 - 200°C	600 - 700°C	650 - 1000°C
System Output	1 - 250kW	10 -100kW	50 –1MW (250kW module typical)	<1kW - 1MW (250kW module typical)	5kW – 3MW
Efficiency	50-60% (electric)	60-70% electric	80 to 85% overall with CHP (36-42% electric)	85% overall with CHP (60% electric)	85% overall with CHP (60% electric)
Applications	• Back-up power • Portable power • Small distributed generation •Transportation	• Military • Space	•Distributed generation	• Electric utility • Large distributed generation	• Auxiliary power • Electric utility • Large distributed generation
Advantages	• Reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Cathode reaction faster in alkaline electrolyte so high performance	• High efficiency •Increased tolerance to impurities in hydrogen • Suitable for CHP	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP
Disadvantages	• Expensive catalysts • High sensitivity to fuel impurities waste heat	• Expensive removal of CO2 from fuel and air streams required	• Requires platinum catalysts • Low current and power • Large size/weight	• Speeds corrosion and breakdown of cell components • Complex electrolyte management • Slow start-up	• Enhances corrosion and breakdown of cell components • Slow start-up

1.8.1 Solid oxide fuel cells (SOFC)

Solid oxide fuel cell technology is a promising source of power generation option in future energy approaches due to its high electrical efficiency and low emission of pollutant such as CO_2, NO_x and SO_x **[120]**. Therefore SOFC appears to be one of the most efficient and effective solution to most of the environmental issues that we face today. Solid oxide fuel cells utilize a hard solid ceramic material as electrolyte and operate at a high temperature (600°C-1000°C) **[120]**. A SOFC is a complex electrochemical device that consists of a porous anode, an electrolyte membrane and a porous cathode.

The high operating temperature (600-1000°C) allows the cell to operate with conventional fossil fuel (as source of H_2 gas) to achieve high efficiency conversion of chemical energy of the fuel to electrical energy and to use in combine heat and power generation or to coupled with a gas turbine. Moreover, high temperature operation enables to speed up the reactions at anode and cathode by removing the need for precious metal (catalyst) and produces high quality by-product heat for co-generation **[119-120]**. Even though high operating temperature is advantageous in many ways, there exist a large number of problems regarding high temperature such as high cost of materials, stability, compatibility and thermal degradation of the materials itself etc. The search of low-cost materials with high durability at higher temperatures is the major technical challenge facing this technology.

There have been two approaches to develop intermediate or low temperature operated SOFC. The simple approach is to reduce the ohmic resistance of the electrolyte by decreasing the thickness, but there are also limitations to this approach **[46]**. For example if we consider a film of thickness 10 μm and a conductivity of $1x10^{-2}$ S/cm corresponding to an area of 0.1 ohm.cm^2 , then the minimum operating temperatures will be ~700°C for YSZ and 550°C for LSGM and CGO **[120]**. Further decrease in thickness cannot further decrease the ohmic resistance. On the other hand, too much reduction in thickness decreases the mechanical strength and may causes failure of the cell operation. Another strategy is to fabricate new electrolyte materials which possess higher ionic conductivity in the lower temperature region. In the recent years,

however, the development of SOFC has been focussed on the latter approach, i.e., on lowering the operating temperature of the electrolyte systems.

1.9 Materials for SOFC components

Due to high operating temperature and multi-component nature of the fuel cell stack, the thrust area, the development of SOFC depends mainly on selection of materials. There are a number of common requirements of cell components such as: stability, matched thermal expansion, reasonable mechanical properties, low vapour pressure and cost competitive fabrication. The following component materials are found to be most suitable for SOFC which have been proved by a number of SOFC manufacturers such as the Global Thermoelectric Company, Westinghouse Electric Corporation, Siemens (now called Siemens Westinghouse Power Corporation) and Fuji Electric [122].

1.9.1 Electrolyte

The electrolytes used in SOFC operation should meet the certain requirements such as high ionic conductivity, low electronic conductivity, stability in both oxidizing and reducing environments, good mechanical properties and long-term stability with respect to dopant segregation. Although a large number of oxide ion conducting ceramics has been developed as active solid electrolyte for SOFC, the extensively studied electrolyte systems are the yttria stabilized zirconia (YSZ), strontium, magnesium doped lanthanum gallate (LSGM) and gadolinium or samarium doped ceria (CGO or CSO) [120]. However, YSZ has emerged as the most common and suitable electrolyte material in SOFC applications. Yttria serves the dual purpose of stabilizing zirconia into the cubic structure at high temperatures and also providing oxygen vacancies at the rate of one vacancy per mole of dopant. A typical dopant level is 10 mol% yttria [122]. Moreover, it fulfils the electrical requirements at high temperature and also possesses good mechanical properties at high temperatures [120-121]. Some other oxide ion conducting solid electrolyte systems which can be used in SOFC are mentioned below [121]:

- Cerium oxide doped with samarium (SDC)
- Cerium oxide doped with gadolinium (GDC)
- Cerium oxide doped with yttrium (YDC)

- Cerium doped with calcium (CDC)
- Lanthanum gallate ceramic that include lanthanum strontium gallium magnesium
- (LSGM)
- Bismuth yttrium oxide (BYO)
- Doped bismuth vanadate (BIMEVOX)
- Barium Cerate (BCN) and
- Strontium Cerate (SYC)

1.9.2 Cathode

Electrodes provide the interface between the chemical energy associated with the oxidation of fuel and electrical power and hence they are vital component in SOFC. In addition to good electrical properties and enough chemical and structural stability, the cathode needed to be porous so that it may allow oxygen molecules to reach the electrode/electrolyte interface. In some cell configurations (e.g. tubular), cathode bear over 90% of the cell's weight and therefore gives the structural support for the cell **[124]**. As the operating temperature of the SOFC is very high, only noble metals or electronic conducting oxide are useful as cathode materials. Noble metals are generally expensive and suffer from the problems regarding long term stability and hence found unsuitable for practical applications **[120]**. The most commonly used cathode material is the lanthanum manganite perovskite ($LaMnO_3$) which provides a good performance at operating temperature above 800^oC. To enhance the ionic conductivity it is generally doped with rare earth elements (eg. Sr, Ce, Pr) and most often it is doped with strontium and referred to as LSM ($La_{1-x}Sr_xMnO_3$). In addition to being compatible with YSZ electrolytes, these perovskites are also found suitable in the intermediate temperatures (about 700 ^oC). Some of the alternative perovskite structured ceramic electrode materials for lower temperature operation are listed below **[121]**:

- o   Lanthanum strontium ferrite (LSF), $(LaSr)(Fe)O_3$
- o   Lanthanum strontium cobaltite (LSC), $(LaSr)CoO_3$
- o   Lanthanum strontium cobaltite ferrite (LSCF), $(LaSr)(CoFe)O_3$
- o   Lanthanum strontium manganite ferrite (LSMF), $(LaSr)(MnFe)O_3$
- o   Samarium strontium cobaltite (SSC), $(SmSr)CoO_3$

o Lanthanum calcium cobaltite ferrite (LCCF), $(LaCa)(CoFe)O_3$

o Praseodymium strontium manganite (PSM), $(PrSr)MnO_3$ and

o Praseodymium strontium manganite ferrite (PSMF), $(PrSr)(MnFe)O_3$

o Further, incorporation of the electrolyte materials into the cathode materials has been reported to improve the cathode performance [121].

1.9.3 Anode

The anode or fuel electrode must satisfy most of the same requirements as the cathode for electrical conductivity, thermal expansion compatibility and porosity, and must function in a reducing atmosphere. Because of the reducing conditions of the fuel gas, metals can be a candidate for SOFC anode materials. Due to the availability and affordability most of the development in respect of cathode materials has been paid on nickel. However, their thermal expansions (13.3×10^{-6}/C compared with 10×10^{-6}/C for YSZ) are too high and have a tendency to sinter and close off its porosity at operation temperature. These problems have been solved by fabricating the anode materials from composite powder mixtures of electrolyte material (YSZ, GDC, or SDC) and nickel oxide NiO which subsequently reduced to nickel metal prior to operation. The YSZ provides structural support for separated Ni particles, preventing them from sintering together and to provide a thermal expansion coefficient comparable to other cell components. [121-122]. NiO/YSZ anode material is suited for applications with YSZ electrolyte materials and NiO/SDC or NiO/GDC anode materials are best used with ceria-based electrolyte materials.

1.9.4 Fuel

SOFC efficiently uses hydrogen as fuel with heat and water as by-product. It requires only a single partial oxidation reformer to pre-process the fuel. The pre-process fuel may be of different kinds of hydrocarbons such as gasoline, diesel, natural gas, etc. The hydrocarbons possess large number of advantages over using hydrogen and also the supply infrastructure for hydrocarbons is presently available. The hydrocarbons can be easily transported and stored because they are in a stable state and need not be processed before use. Moreover, they are also more capable of producing energy. Methane for example has eight electrons per molecule but hydrogen yields only two

electrons. With the use of more complex hydrocarbons (e.g. pentane), this benefit could increased to a larger extent **[121]**.

1.10 Application of SOFC

The solid oxide fuel cell (SOFC) is a promising power generation option for future energy approaches due to its high energy conversion efficiency and low emissions of gases **[119-120]**. SOFCs have the ability to utilize a large variety of currently available fossil fuels such as methane and natural gas with high efficiency and thus reducing the operating cost **[122]**. SOFC systems can have wide applications ranging from portable /emergency power generators, small scale power systems (residential or automobile auxiliary power units) to large scale power plants **[121-125]**. The SOFC is the only type of fuel cell which has such a wide range of applications. Some of the SOFC power systems concepts are discussed below **[125]**.

(i)   20-W portable system: This system is a thermally integrated unit which includes an SOFC operating on jet fuels (JP-8). This system weighs about 0.6 kg (without fuel) in a volume of 3.3 by 4.5 by 7.9 in. (8.5 by 11.5 by 20 cm) and is designed to produce 20 W at 12 VDC.

(ii)   500-W portable system: The portable 500-W battery charging system operating on logistic fuels (JP-8) is generally used for military applications. The system produces 28 V and is estimated to weigh 7 kg in a volume of 17 by 11 by 9 in. (43 by 28 by 23 cm).

(iii)   kW power system: This system has the all necessary components for a self-contained unit, including SOFC stack, fuel processing subsystem, fuel and oxidant delivery subsystems, thermal management subsystem, and various control and regulating devices. The design of a 5-kW system has also been developed for automobile auxiliary power units (APUs). Stationary kW size systems have been demonstrated.

(iv)   100–250 kW combined heat and power (CHP) SOFC system: Several CHP systems (100 to 250 kW) has been developed and operated. For example, a 100-kW unit operated for more than 20,000 h at 110 kW net AC and 46% electrical efficiency.

(v)   Multi-MW SOFC/gas turbine (GT) hybrid system: Highly efficient multi-MW hybrid systems (up to 70% system efficiency) can be formed by

integrating SOFCs with gas turbine. In such a system, the left over fuel from the fuel cell is burned by the gas turbine to produce extra electricity. Based on the type of the hybrid system (directly fired turbine or indirectly fired turbine), either a pressurized or an atmospheric SOFC is used. Pressurized SOFC/GT systems have been built and operated.

1.11 Status of SOFC development and markets

The most recent effort in SOFC development started in the USA and Japan, Europe, Australia in 1985, 1989 and 1991 respectively. A large number of companies and government research organizations worldwide are involved in R&D programs on SOFC development, supported largely by public funding agencies (DOE, GRI, MITI, CEC). Westinghouse is generally regarded as the world leader in SOFC development **[126]**. The company has developed the tubular concept to an advanced state, having built a 40 kW prototype unit. Other players (Siemens, Ceramatec, Fuji Electric, Sanyo and Sulzer) are developing planar stacks with either metallic or ceramic interconnects and units up to 1 kW have been constructed. Mitsubishi Heavy Industries is developing tubular, planar and a monolithic/planar hybrid design and has constructed 1 kW units for each design. In Australia, a SOFC development project started in CSIRO-DMST in 1991. In 1992 a consortium consisting of CSIRO, major utilities, BHP and government R&D funding bodies established Ceramic Fuel Cells Ltd. The company focuses on development of materials and cost effective fabrication technology for planar SOFC stacks.

A large number of companies are engaged in SOFC development. The following tables (table 1.2(a) to 1.2(c) list the most important developers.

Table-1.2 (a): Fuel cell developers in Europe [**127**].

Country	Institution/Company	Concept	Main focus in development
Denmark	Haldor Topsoe together with Risoe	Planar: until 1999: ceramic IC, electrolyte substrate since 2000:metallic IC, anode substrate	System, reformer materials, cells, stack
Finland	VIT	---------	Fuel conditioning, cell and stack testing, modeling
	Wartsil	---------	system
Germany	BMW	Planar, metallic IC, metallic substrate	Stack, system
	DLR-Stutigart	Planar, metallic IC, metallic substrate	Materials, cells, stack
	FZJ	Planar, metallic IC, metallic substrate	Materials, cells, stack, system modeling
	H.C.Stack,/Iodec (NL)	---------	Powders, cell manufacturing
	IKTS-Dresden	Planar, metallic IC, electrolyte substrate	stack
	Siemens	Tubular. "flat tube"	Materials, manufacturing
	Webasto	Planar, metallic IC, electrolyte substrate	Stack, system
	EDF/GDF		Fuel conditioning, testing
	CEA; Fuel Network		materials
Great Britain	Cerca Power	Planar, CGO electrolyte for 550 ^{O}C, metallic IC, metallic substrate	Materials, cells, stack, system
	Rolls Royce	Planar, on porous ceramic substrate	Materials, cells, stack, system
Netherlands	ECN	---------	Materials, cells, stack
Switzerland	Sulzer Hexis	Planar, metallic IC, electrolyte substrate, anode substrate	Materials, cells, stack, system
Europe		Total employee (ca.)	450-500

Table-1.2 (b): Fuel cell developers in North America [**127**].

Country	Institution/Company	Concept	Main focus in development
USA	Acumentrics	Tubular (anode substrate)	Cells, stack, system
	ANL (Argonne National Lab.)	Planar, metallic IC, electrolyte substrate	Materials, cells, modeling
	Cummings/SOFCo	Planar, ceramic IC, electrolyte substrate	Materials, cells, stack, system
	Delphi Automotive Systems (collaboration with PNNL)	Planar, metallic IC, anode substrate	cells, stack, system/APU
	GE (former Honeywell former Allied Signal)	Planar, metallic IC, anode substrate	Materials, cells, stack, reformer.
	LLNL (Laurence Livermore National Lab.)	Planar, metallic IC, anode substrate	cells, stack
	NETL (National Energy Technology Lab.)	---------	
	PNNL (Pacific Northwest National Lab.)	Planar, metallic IC, anode substrate	Materials, cells, modeling
	SWPC	Tubular (cathode substrate); "flat tube"	cells, Stack, System
	ZTek	Planar, metallic IC	cells, Stack, System
Canada	Global Thermoelectric (now part of Versa Power)	Planar, metallic IC, anode substrate	Materials, cells, stack, system
	FCT (Fuel Cell Technology) together with SWPC	---------	system
North America		total employee (ca.)	450-500

Table-1.2(c): Fuel cell developers in Asia and Australia [**127**].

Country	Institution/Company	Concept	Main focus in development
Japan	Kyocera with Tokyo Gas and Osaka Gas	Cylindrical planar flat tubular (anode substrate) "horizontal pattern"	Materials, cells, stack, system
	Mitsubishi Heavy Industries (MHI) with Chubu EPDC	Tubular (porous support tube, serial connection)	Materials, cells, stack, system
	Mitsubishi Heavy Industries (MHI) with Chubu EPCo (CEPCo)	MOLB Design: planar, ceramic IC, electrolyte substrate	Materials, cells, stack, system
	Mitsubishi Materials(MMC) with Kyushu EPCo (PEPCo)	Gallate electrolyte, 800 ^{O}C planar, metallic IC, electrolyte substrate	Materials, cells, stack, system
	Nihon Gaihi (NGK)	Planar, anode substrate	Materials, cells
	Nippon Shukubai	Planar, electrolyte substrate	Materials, cells
	Tobo Gas	Planar, metallic IC, anode substrate	Materials, cells, stack, system
	TOTO with Kyushu EPCo (KEPCo)	Tubular (cathode substrate)	Materials, cells, stack, system
Korea	KIER (Korean Institute of Energy research)	Anode supported flat tube	Stack, system (pressurized)
Australia	CFCL	Planar, electrolyte substate, since 2001 shift to ceramic IC	Materials, cells, stack, system
Asia, Australia		Total employee (ca.)	350-400

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