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Solid Electrolytes

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ABSTRACT

Solid State Ionics continues to be a rapidly developing research field because they exhibit high ionic conductivity; negligible electronic conductivity and low value of activation energy for ion migration at temperatures below their melting point are known as Solid Electrolytes (SEs) or Super Ionic Conductors (SICs) or Fast Ion Conductors (FICs). These solid electrolytes created a great deal of attention in modern researchers because of their unique transport properties and potential applications. This paper mainly explains about various types of solid electrolytes (conductivity values) and their various applications in solid state electrochemical devices such as rechargeable batteries, electro-chromic displays, solid state sensors, super capacitors thermoelectric devices, fuel cells, solar cells, memory devices and high energy storage batteries discussed.

Keywords: Ionic Conductivity, Fuel Cells, Solar Cells

I. INTRODUCTION

The word "ion" originated from a Greek word "ιον", which means "going" or "moving thing" in Greece and it was first introduced by Michael Faraday in 1834 [1]. The term "solid state ionics" was initiated in 1960 by Takehiko Takahashi, who did pioneering work in the field of ionics [2]. After a long gap, about more than a century, 1967 can be considered as the beginning of the field of solid state ionics because of discovery of high ion conducting two groups of solids: MAg_4I_5 (M = Rb, K, NH_4) [3] Study of solid state ionics has attracted very interest in material scientists for the last few decades, because of their potential applications in solid state ionic devices such as rechargeable batteries, electro-chromic displays, solid state sensors, thermoelectric devices, fuel cells, memory devices and high energy storage batteries [4]. The reported major problems of liquid electrolytes are (1) cell liquid leakage (2) corrosion (3) self-discharge process (4) drying out of the cell (5) loss of electrolyte (6) limited temperature range of operation (7) bulky in size and (8) severe restrictions on the capability of useful discharge at very low temperatures [5]. The ionic conductivity of some solids is exceptionally high comparable to that of liquid/aqueous electrolytes. Therefore, these solids can be potentially utilized as excellent replacement with liquid/aqueous electrolytes to fabricate solid state electrochemical devices. The main advantages of solid materials in power source devices are to minimize irreversible losses arising from the high internal resistances, long life, high energy density, miniaturization of electronic devices, design flexibility and operate the electrochemical device at high temperatures.

Also, a good solid electrolyte should have the following characteristics:

1) Ionic crystal bonding.
2) High electrical (ionic) conductivity [10^{-1} - 10^{-4} ohm^{-1} cm^{-1}].
3) Ions being the principal charge carriers which means that ionic transport number [t_{ion}] is almost equal to 1.
4) Negligible electronic conductivity. Generally materials with electronic transport number [t_e] less than 10^{-4} are considered as good solid electrolytes.
5) Stability with respect to adjacent phases and to thermal and electrochemical decomposition
6) Suitable mechanical properties
7) Ready availability of chemical constituents
8) Ease of fabrication, and
9) Reasonable cost [6].

Mainly solids ionic conduction can take place either by hopping of ions through a series of interstitial sites or vacancy sites (Frenkel defect) or by hopping of pair of ions through vacancies in the lattice (Schottky defect)

1.1 Broad Classification of Solid Electrolytes:

Solid electrolytes are broadly classified based on the physical properties, microstructures and synthesis routes as mentioned below:

- ✓ Framework crystalline / single crystalline/ polycrystalline solid electrolytes
- ✓ Glassy / amorphous solid electrolytes
- ✓ Polymer electrolytes
- ✓ Composite solid electrolytes

Further the composite solid electrolytes can again be classified as

(i) Crystal-crystal composites
(ii) Crystal-glass composites
(iii) Glass-polymer composites and
(iv) Crystal-polymer composites [7]

These types of solid electrolytes can have either ordered or disordered phases. Framework crystalline materials are in ordered phase whereas the three remaining solid electrolytes are in disordered phase

1.1.1 Framework / single crystalline /polycrystalline solid electrolytes:

Framework crystalline electrolytes, as the name implies, consist of a crystalline skeleton of more or less rigid and mobile ions. In the beginning of field of ionics, it was believed that a solid material with rigid crystal structure cannot conduct much through movement of ions. But, the discovery of large electrical conductivity in AgI [8], MAg_4I_5 (M = Rb, K, NH_4) [3-4], Na-β- alumina [9], doped Zirconia [10] solid materials shows that the rigid crystal structures/ framework crystals are also good ionic conductors like liquid electrolytes. Crystalline materials of both cations and anions as mobile ions (Ag^+, Cu^+, Li^+, Na^+, H^+ O^{2-}, F^-, Cl^-, NO_3^- etc.) have been reported [11]

1.1.2 Glassy/amorphous solid electrolytes:

Fast ion conduction in glassy/amorphous solid electrolytes was highlighted in the later part of 1970's. Superionic conducting glasses are suitable materials for solid-state electrical devices because of its thermodynamic properties of high random free energy for the motion of the carrier ion compared to their respective crystalline counterpart Some important advantages include high isotropic ionic conduction, absence of grain boundary conduction, wide range of compositional variability, chemical durability and thereby obtaining range of property control, ease of preparation into desirable shapes with the possibility to form thin films, potential electrochemical applications, etc. [12].

1.1.3 Polymer Electrolytes

Polymer electrolytes, a novel class of materials attracting tremendous technological interest in the recent years, are electro-active polymers with moderately high ionic conductivity ($\sigma \sim \leq 10^{-4}$ Scm^{-1}) at room temperature. High ionic conducting polymer solid electrolyte (PSEs) was first reported by Fenton et al [13].

1.1.4 Composite solid electrolytes:

Solid electrolytes containing dispersed second phase insulating and chemically inert particles are called composite solid electrolytes or dispersed solid electrolytes. Composite solid electrolytes are high ion conducting multiphase solid systems created a center of attraction. They are mostly two-phase mixture, containing a moderately conducting ionic solid such as $NaNO_3$, AgI, CuI etc. as first phase host salt and a second phase material, such as Al_2O_3, SiO_2, ZrO_2, CeO_2, Fe_2O_3 etc or another low conducting ionic solid such as AgBr, AgCl, KCl etc Survey of the literature showed that the conduction mechanism in the most of crystal-crystal composites was of vacancy or interstitial type or Frenkel or anti Frenkel type, which was explained using space charge model by anion or cation adsorption. It was also noticed that the combination of homogeneous and heterogeneous doping was consistent in these systems [14].

(i) Crystal-glass composites :

In these crystal-glass composites, there is dispersion of insulating, insoluble and chemically inert non-crystalline particles such as Al_2O_3, SiO_2, fly-ash into the ionic solid of first crystalline phase to increase the ionic conductivity. In these composites, the first phase ionic solid is crystalline in nature, whereas insulating particles are amorphous in nature. The enhancement in conductivity in the most of crystal- glass composites is due to the increased defect concentration in the interfaces in between the ionic solid and nano-particles [15].

(ii) Crystal-polymer composites:

The crystal-polymer composites are the conventional solid polymer electrolytes (SPEs) with filler particles of organic/ inorganic materials such as polymers like polystyrene, PMMA, PAA, PVA

(iii) Glass-polymer composites:

The Glass-polymer composites are the conventional solid polymer electrolytes (SPEs) dispersed with ion conducting glasses viz. (Li_2O: B_2O_3), $LiBF_4$, (Na_2O: B_2O_3), (LiI: B_2S_3), (LiI: Li2S: B_2S_3) etc [16].

1.2 Applications of Solid Electrolytes:

The first application of solid electrolytes was demonstrated by Nernst, utilizing zirconium dioxide in a device known as "Nernst glower" for light emission. A brief review on various application aspects of these materials has been made in this section.

1.2.1 Solid State Batteries:

Batteries are often use in micro-electronics to operate cars/ cameras/ toys/ watches/ mobile phones/ laptops etc. These batteries are fabricated in a wide range of energy to cater different power requirements. Battery is the electrochemical device and that converts chemical energy into electrical energy. The major components required to manufacture the battery are an electrolyte, two electrodes i.e. an active anode and cathode.

1.2.2 Electro-chromic Display (ECD) Devices:

Electro-chromic Displays (ECDs) are the most recent addition to the list of display devices such as Light-Emitting Diodes (LEDs), Liquid Crystal Displays (LCDs) etc. Broadly, electro-chromic defined as colour change induced in a material by an applied electric field or current. Superionic solids can be used as ion reservoirs in place of liquid electrolytes.

1.2.3 Fuel Cells:

A fuel cell is an electrochemical device which also converts free energy of a chemical reaction into electrical energy by a process involving essentially invariant electrode-electrolyte systems. Fuel cell and battery both are similar, but external fuel is supplied to fuel cell, while a battery consumes internal fuels to generate electricity. A fuel cell can produce electricity continuously as long as the fuel is supplied; in contrast a battery needs to be recharged once the internal fuel is used up.

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