

# Chapter 1

## Introduction

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### 1.1. General Introduction

In the current society, haphazard exploitation of fossil fuels (coal, petroleum, natural gas) has resulted in heavily irreversible hazards, including environmental pollution, resource scarcity, and global warming, which has acted as an obstacle to the sustainable development of society [1]. In recent times, non-conventional energy sources viz. wind, solar, and tidal energy have been explored extensively as an alternative to satisfy societal needs. To store any of these intermittent energies most effectively, electrochemical energy storage systems are the favored technology. Lead-acid battery technology developed almost 150 years back has dominated the commercial battery market so far. Ever since Sony commercialized the world's first rechargeable Li-ion battery (LIB) in the 1990s [2], significant academic and commercial progress has been made on LIBs. In the past decades, rechargeable lithium-ion batteries (LIBs) along with lithium-ion capacitors (LICs) leading to high energy density and high power density, respectively have dominated the vast market of electrochemical energy storage devices involving laptops, communication, consumer electronics, and electric vehicles (EVs) due to their high shelf-life and stable cycling performance [3].

The current LIBs and other batteries in the market still use toxic liquid/gel electrolytes that lead to several environment-related concerns, therefore, need a restriction on large-scale use in various future applications e.g. EVs, microgrids. The liquid/gel used in the device leads to leakage, restricted stability with temperature, and flammability. Further, the low dimensional systems (e.g. micro batteries) cannot be realized using current generation liquid electrolytes. Solid electrolytes (SEs) has become an accepted alternative strategy to overcome these issues [1][4]. In contrast to liquid/gel electrolytes, solid electrolytes are generally nontoxic, usually demonstrate the specific advantages of a non-leakage, wide electrochemical window, superior thermal stability, and mechanical strength. Thus, with the emergence of a novel research area

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of solid state ionics [5], fast ionic solids have been widely studied in the last four decades due to their potential candidature for all-solid-state ionic devices [6][7]. Broadly solid electrolytes can be categorized into inorganic and organic fast ionic solids (FICs). Among the various inorganic FICs, garnet oxides, sodium superionic conductors (NASICONs), and sulfides along with some more compounds exhibiting such open structures suitable for fast ionic transport have been widely explored because of their high in-grain ionic conductivity, along with ionic transport number near unity. Though, these electrolytes have some major issues such as high grain boundary impedance (GBI) at ambient temperatures and poor interfacial compatibility with electrodes. On the other hand, organic polymer electrolytes can be prepared with relatively simple processing route and also cost-effective. These have also been studied due to their flexibility and interfacial compatibility. Nevertheless, issues e.g. inadequate ionic conductivity at room temperature finally restrict the realization of commercial all-solid-state batteries (ASSB) and other devices. The further discussion in the chapter is thus focused on solid polymer electrolytes (SPEs) given the nature of the work undertaken in the thesis.

### 1.2. Solid polymer electrolytes (SPEs)

Owing to several advantages over liquid or gels, solid polymer electrolytes (SPEs) have attracted the ever-increasing interest in the field of  $\text{Li}^+$  ion batteries, fuel cells, supercapacitors, etc. As stated earlier SPEs offer a relatively stable electrode-electrolyte interface, improved safety features, excellent flexibility, and processability [3]. Moreover, there are some critical issues in the case of liquid electrolytes such as dendrite formation that could be minimized using SPEs [8]. The first ion conducting SPE with alkali metal salts was first reported by . After few years, M. Armand et. al. [10] boosted the interest in these materials by targeting their use in electrochemical devices, especially  $\text{Li}^+$  ion/lithium batteries. The same group is also given the credit for the pioneering work of proposing a mechanism of ionic transport in SPEs. According to this, amorphous regions in the polyethylene oxide (PEO, host polymer) are essentially responsible for fast ionic transport. This proposition subsequently directed efforts into increasing these amorphous domains in the bulk materials by suppression of crystallinity. Since then, there have been substantial efforts towards the development of various novel solid polymer electrolytes and theoretical modeling of their ion transfer mechanism, along with the physical and chemical properties of the electrolyte/electrode interface. So far, different forms of  $\text{Li}^+/\text{Na}^+$  ion based polymer complexes have been developed

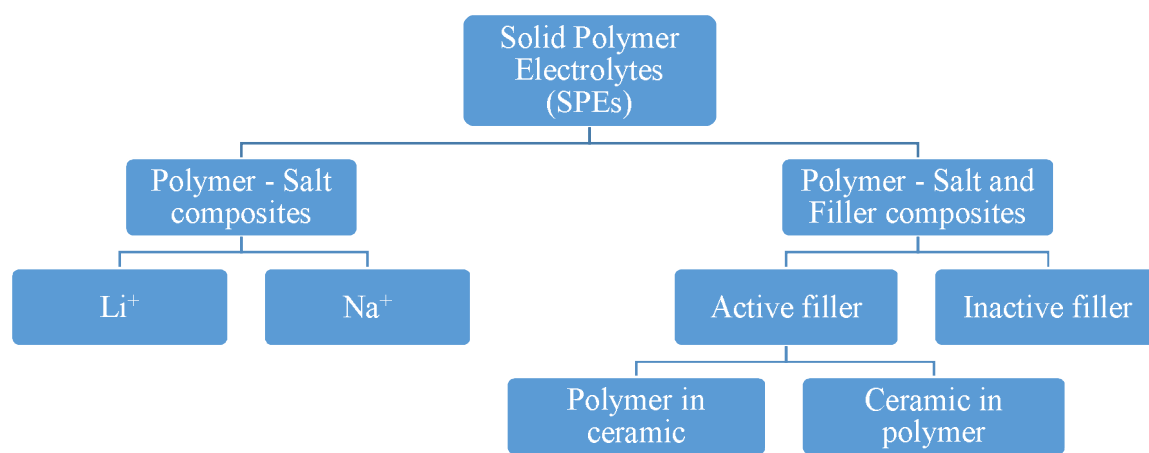
and explored for electrolytic applications. The properties of these SPEs are dictated to a great extent by the host polymer matrix. Some of the reported polymer backbones (the host) along with their physicochemical properties are given in Table. 1.1.

**Table.1.1** Different types of polymer hosts along with their physicochemical properties.

Polymer	Monomer	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Cathodic stability
PEO (Polyethylene Oxide)	$\left( \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}-\text{O}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right)_n$	-64	65	Stable
PVC (Polyvinyl Chloride)	$\left( \begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right)_n$	80	220	Poor
PAN (Polyacrylonitrile)	$\left( \begin{array}{c} \text{H} \quad \text{CN} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right)_n$	125	317	Poor
PMMA (Poly methyl methacrylate)	$\left( \begin{array}{c} \text{H} \quad \text{COOCH}_3 \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array} \right)_n$	105	Amorphous	Stable
PVdF (Polyvinylidene fluoride)	$\left( \begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \right)_n$	-40	171	Poor
P(VDF-HFP) <b>Poly</b> (vinylidene fluoride-co- hexafluoropropylene)	$\left( \begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \right)_n \left( \begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{CF}_3 \end{array} \right)_m$	-90	135	Poor

Among various polymer electrolytes, polyethylene oxide (PEO) has been widely studied because of its ability to solvate a variety of salts through coordination between cations and ether oxygen (CH<sub>2</sub>-CH<sub>2</sub>-O) of polymer chains [11]. To overcome the issues related to poor conductivity, several investigations have been focused on enhancing electrical transport along with achieving better cation transference (t<sub>+</sub>) numbers. Further, several studies on blended polymers with plasticizers have also been reported [12][13][14]. Plasticizers are low molecular weight, nonvolatile substances that, when added to a polymer, improve its flexibility, processability, and, hence utility. Mostly, low molecular weight, high dielectric constant polar organic solvents such as ethylene carbonate (EC), propylene carbonate (PC), polyethylene glycol (PEG) have been used as plasticizers. The incorporation of a plasticizer in polymer

electrolytes influences the ionic conductivity in two important ways: firstly by increasing the polymer chain mobility; and second, by creating a ‘liquid like’ phase within the polymer. Nevertheless, such high ionic conductivity is certainly on the cost of mechanical strength. Consequently, it was realized to have a more effective strategy for balancing mechanical and electrochemical properties. Efforts were still on in this direction, until the development of SPEs based on nano fillers (Fig. 1.1). Discussion on  $\text{Na}^+/\text{Li}^+$  ion-based SPEs here onwards will be focused on filler-based SPEs, given the orientation of the current work.



**Figure 1.1** Schematic diagram showing the different forms of solid polymer electrolytes (SPEs)

### 1.3. Polymer-salts complexes

#### 1.3.1. $\text{Li}^+$ ion systems

Several attempts have been made to enhance the ionic conductivity in SPEs by increasing salts concentration in the matrix. As discussed earlier, such approaches certainly provided high ionic conductivity, but at the cost of mechanical strength. Further, the concentration of the salts in the matrix had a constraint due to the solvation limit. It was soon realized that an increase in a salt concentration above a certain limit leads to a decrease in ionic conductivity, as the ion association in the polymer complexes initiates with the reduction in vacant coordination sites [15].

Various groups have reported the complexation of different  $\text{Li}^+$  ion conducting alkali metal salts with polymer PEO. The ionic conductivity of such complexes is seen to be influenced by the anionic size. This is because the criterion of lattice energy has to be fulfilled for forming complexes with cations, especially  $\text{Li}^+$  ions. Furthermore, anion with larger ionic radii

possesses the least lattice energy, and those with low charge density have the least tendency to form tight ion pairs [2]. Some of the most widely used lithium salts are LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, etc. The mobility of the ions and their dissociation constant are reported in the following order for various salts [2]:

Mobility of ions: LiBF<sub>4</sub> > LiClO<sub>4</sub> > LiPF<sub>6</sub> > LiAsF<sub>6</sub> > LiCF<sub>3</sub>SO<sub>3</sub> > LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>

Dissociation constants: LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> > LiAsF<sub>6</sub> > LiPF<sub>6</sub> > LiClO<sub>4</sub> > LiBF<sub>4</sub> > LiCF<sub>3</sub>SO<sub>3</sub>

Some of the anions for Li<sup>+</sup> ion conducting salt complexes with polymer PEO matrix, along with their ionic conductivity are shown in Table 1.2.

**Table 1.2** Various polymer-Salt complexes as reported.

Composition	Ionic conductivity ( $\Omega^{-1}\text{cm}^{-1}$ ) at 25-30 °C	Important observations	Reference
P(EO) <sub>20</sub> -LiBF <sub>4</sub>	$6.32 \times 10^{-7}$	Effect of anion size on dc conductivity	Choudhary et. al (2012) [16]
P(EO) <sub>20</sub> -LiClO <sub>4</sub>	$2.78 \times 10^{-7}$		
PEO-15 wt% LiPF <sub>6</sub>	$1.82 \times 10^{-5}$	Bayesian Neural network to predict salt conc.	Ibrahim et. al (2011) [17]
PEO-15 wt% LiCF <sub>3</sub> SO <sub>3</sub>	$1.00 \times 10^{-6}$	Ion aggregation at higher salt conc.	Klongkan et. al. (2015) [18]
PEO <sub>20</sub> LiN(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	$\sim 10^{-6}$	ESW of 4.4V vs Li/Li <sup>+</sup>	Zhao et. al. (2006) [19]
90PEO-10LiAsF	$1.43 \times 10^{-4}$	Aggregation of salt after 10 wt%	Reddy et.al. (2007) [20]
PEO <sub>12</sub> -LiI	$\sim 10^{-6}$	Introduction of CdO to enhance dc conductivity	Karmakar et. al (2011) [21]

### 1.3.2. Na<sup>+</sup> ion systems

With the ever-increasing demand and depletion of lithium resources (0.0017 wt%), practical applications to large-scale grid storage and sustainable development in real society have been

plagued. Therefore, exploring next-generation charge storage devices is an important and urgent issue [22]. Although Na<sup>+</sup> ions (- 2.71 V vs. SHE (Standard Hydrogen Electrode) for Na<sup>+</sup>/Na) display a little higher reduction potential than Li<sup>+</sup> ions (- 3.04 V vs. SHE for Li<sup>+</sup>/Li), Na<sup>+</sup> ion based energy storage devices including batteries and supercapacitors recently attracted widespread attention due to the abundant reserves of Na (2.36 w%) [23][24].

In a similar line with that of Li<sup>+</sup> ion conducting solid polymer electrolytes, several studies have been reported on polymer (PEO) complexes with Na<sup>+</sup> ion alkali metal salts. Research on ambient temperature operating sodium batteries started in the 1980s and 90s [25]. After that several sodium salts have also been examined for PEO-based SPEs, including NaPF<sub>6</sub>, NaClO<sub>4</sub>, NaCF<sub>3</sub>SO<sub>3</sub>, NaSCN, NaNO<sub>3</sub>, NaBF<sub>4</sub>, sodium 2,3,4,5-tetracyanopirolate (NaTCP), sodium 2,4,5-tricyanoimidazolate (NaTIM), etc. Table 1.3 shows some of the reported polymer PEO complexes with Na<sup>+</sup> ion conducting alkali salts along with their ionic conductivity.

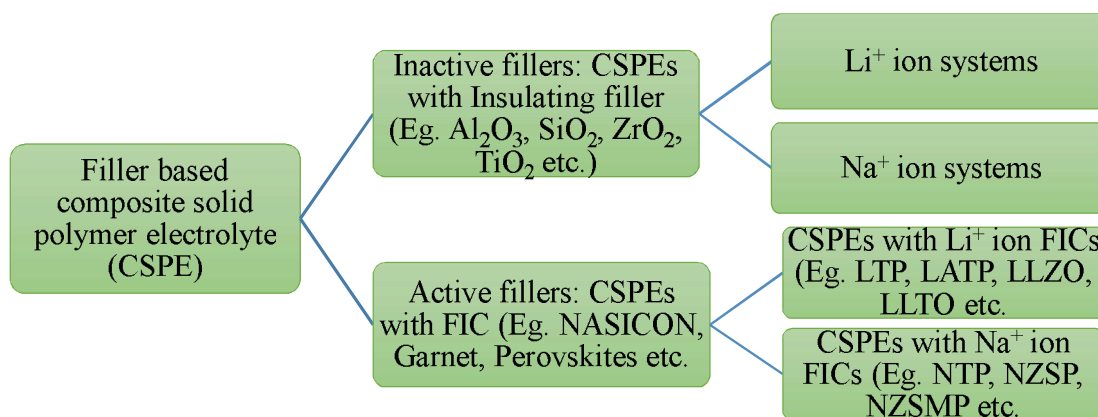
**Table 1.3** Electrical properties of some important Na<sup>+</sup> ion conducting polymer-alkali salts complexes electrolytes. ESW, OCV, and SSC stand for electrochemical stability window, open-circuit voltage, and short circuit current, respectively.

Composition	Ionic conductivity ( $\Omega^{-1}\text{cm}^{-1}$ )	Important observations	Reference
PEO-NaPF <sub>6</sub>	$6.3 \times 10^{-4}$ (80°C)	ESW of 4.5 V vs Na/Na <sup>+</sup>	Zhang et. al. (2020) [26]
PEO-25 wt% NaClO <sub>3</sub>	$1.53 \times 10^{-5}$ (50°C)	Ion aggregation at high salt content.	Rajendra et. al. (2013) [27]
70PEO-30 NaNO <sub>3</sub>	$2.83 \times 10^{-6}$ (30°C)	OCV and SCC as 2.61 V and 1.35 mA	Sreekanth et. al. (1999) [28]
PEO20-NaClO <sub>4</sub>	$1.35 \times 10^{-4}$ (60°C)	Ion aggregation and poor mechanical strength at high salt conc.	Nimah et. al. (2015) [29]
PEO-NaTFSI	$4.5 \times 10^{-6}$ (27°C)	$t_{\text{Na}^+} = 0.39$ , ESW = 4.8V	Moreno et. al. (2014) [30]

PEO <sub>20</sub> _NaFSI	4.1 x 10 <sup>-4</sup> (80°C)	ESW of 4.66 V vs Na/Na <sup>+</sup> Good cycling with NVP	Qi et. al. (2016) [31]
PEO-NaFNFSI	2 x 10 <sup>-6</sup> (27°C)	ESW of 4.87 V vs Na/Na <sup>+</sup> , Current density of 122.4 mAhg <sup>-1</sup>	Ma et. al. (2017) [32]
PEO <sub>6</sub> -NaPO <sub>3</sub>	2.8 x 10 <sup>-8</sup> (80°C)	Ion aggregation at high salt concn.	Bhide et. al. (2006) [33]

#### 1.4. Composite solid polymer electrolytes (CPEs)

It is noticeable that polymer (PEO) complexes with Li<sup>+</sup> ion conducting salts usually display very low ionic conductivity at ambient temperature, which excludes them from practical applications. Among the various approaches, incorporating inorganic fillers into solid polymer electrolytes to prepare composite solid polymer electrolytes (CSPEs) was not only found to be an effective way to enhance their ionic conductivity, but also electrochemical stability, as well as mechanical strength. These systems are further elaborated as shown schematically in Fig. 1.2.



**Figure 1.2** Different types of composite solid polymer electrolytes (CSPEs) explored by various groups.

In general, inorganic fillers can be classified into two types: inactive and active fillers. Inactive fillers, such as inert ceramics, oxygen-ion conducting ceramics, ferroelectric ceramics, and clays with small crystallite size, cannot directly offer transport pathways for Li<sup>+</sup> ions in

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electrolytes but can facilitate  $\text{Li}^+$  transport *via* amorphization of polymers [34]. While active ceramic fillers, e.g.  $\text{Li}_3\text{N}$ ,  $\text{Li}_{7-x}\text{La}_3\text{Zr}_{12-x}\text{Ta}_x\text{O}_{12}$  [35],  $\text{Li}_{3-2x}(\text{Al}_{1-x}\text{Ti}_x)_2(\text{PO}_4)_3$  [36],  $\text{Li}_x\text{La}_{2/3-x}\text{TiO}_3$  [37] and  $\text{Li}_{1.6}\text{Al}_{0.6}\text{Ge}_{0.8}(\text{PO}_4)_3$  [38]), are well known fast Li-ion conductors, which can exhibit high ionic conductivity and  $\text{Li}^+$  transference number. Moreover, inorganic fillers with various morphologies, such as nanoparticles, nanowires, nanofibers, and three-dimensional (3D) frameworks, have also been explored to improve the mechanical and electrochemical properties of CPEs. In the past two decades, inorganic fillers have been preferred widely for designing high-performance CPEs. The details on the influences of category, nanostructure, size, and concentration of inorganic fillers for  $\text{Li}^+/\text{Na}^+$  ion-conducting system on the performance of CPEs will be discussed in the next section.

#### 1.4.1. Composite polymer electrolyte with inactive fillers

Introducing inorganic fillers into polymer matrices has been treated as an elegant approach to enhance the ionic conductivity of electrolytes mainly due to, (i) the crystallinity and glass transition temperature ( $T_g$ ) can be reduced after the addition of inorganic fillers; and (ii) the surface groups of inorganic fillers can interact with polymer chains and salts, to facilitate faster ion conduction throughout the conductive pathways on the inorganic surfaces. Several studies have revealed that the addition of insulating nanoparticles in polymer solid electrolytes affects ionic conductivity significantly. This is because, the addition of nanoparticles reduces the degree of order of the polymer chains, and enhances their segment motion [34]. This further inhibits the polymer crystallization, increases the proportion of amorphous regions, thereby improves the ionic transport [34]. Also, the interaction of Lewis-acid groups on the surface of nanoparticles with polymers and salts limits the migration of anions and enhances the transport capacity of  $\text{Li}^+$  [39][40] ions. In addition, the uniformly distributed nanoparticles also improve the mechanical strength of the electrolyte, strengthen the thermal and electrochemical stability, along with electrode/polymer electrolyte interface stability. In most cases, an adequate mass fraction of nanoparticles in the matrix is limited to ~10-15 wt% [27-31]. Further higher wt% leads to reduction of the polymer itself and this leads to agglomeration of the nanoparticles, resulting in blockage and destruction of the ion conduction pathways, which causes a reduction in the ion conductivity. Some of the reported  $\text{Li}^+$  ion conducting CPEs are given in the Table.

1.4.



**Table 1.4** Li<sup>+</sup> ion conducting composite polymer electrolytes containing inactive fillers

Composition	Ionic conductivity ( $\Omega^{-1}\text{cm}^{-1}$ ) at 30°C	Important observations	Reference
PEO <sub>20</sub> -LiCF <sub>3</sub> SO <sub>3</sub> -8 wt% ZrO <sub>2</sub>	$2.04 \times 10^{-5}$	Decoupling between structural and conductivity relaxation	Dam et. al. (2016) [41]
PEO-15 wt% LiCF <sub>3</sub> SO <sub>3</sub> -20 wt% Al <sub>2</sub> O <sub>3</sub>	$8.64 \times 10^{-5}$	With high filler content, strength, elongation and young's modulus of CSPEs dropped	Klongkan et. al. (2015) [18]
P(EO) <sub>8</sub> -LiClO <sub>4</sub> -10 wt% Al <sub>2</sub> O <sub>3</sub>	$10^{-5}$	$t_{\text{Li}^+} = 0.31$	Croce et. al. (1998) [42]
P(EO) <sub>8</sub> /LiClO <sub>4</sub> /10 wt% TiO <sub>2</sub>	$2.3 \times 10^{-5}$	$t_{\text{Li}^+} = 0.5-0.6$ , Cycling efficiency of 99%	Croce et. al. (2000) [43]
P(EO) <sub>16</sub> -LiClO <sub>4</sub> -10 wt% SiO <sub>2</sub>	$10^{-5.5}$	ESW = 5.0V, Improved dc conductivity with surface modified filler	Fan et. al. (2003) [44]
PEO-LiClO <sub>4</sub> -10 wt% SiO <sub>2</sub> nanospheres	$4.4 \times 10^{-5.5}$	ESW = 5.5 vs Li <sup>+</sup> /Li, 170 mA <sub>g</sub> <sup>-1</sup> in LFP/CPEs/Li cell	Lin et. al. (2016) [45]

Similarly, conventional inactive fillers such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and BaTiO<sub>3</sub> etc. have also been employed to prepare the Na<sup>+</sup> ion-based CSPEs. For example, a PEO-based CSPE containing NaClO<sub>4</sub> and nano-sized TiO<sub>2</sub> (3.4 nm) was synthesized by Ni'mah et. al. [29]. At 60°C, the ionic conductivity of  $2.6 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  was obtained when 5 wt% TiO<sub>2</sub> was added into the matrix. The improvement of ionic conductivity can be ascribed to the decreased crystallinity of PEO phase, enabling faster ionic transport. Chen et al. [46] also demonstrated the enhancement of ionic conductivity in polymer electrolytes with the addition of nano-sized

Al<sub>2</sub>O<sub>3</sub> fillers. The PMA-based CSPE having 3 wt%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> showed an ionic conductivity of  $1.5 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ , and also high anodic stability of 4.5 V at 70°C.

Such dispersion of insulating nanofillers actually leads to a remarkable rise in ionic conductivity in Na<sup>+</sup> as well as Li<sup>+</sup> ion CSPEs, additionally also offers mechanical strength to these systems. Nevertheless, such an enhancement is limited to a certain extent due to the amount and size of fillers. With large content, insulating fillers act as obstacles to the motion of mobile ions and hence degrade the overall ionic conductivity. Some of the reported Na<sup>+</sup> ion SPEs with inactive fillers is shown in Table 1.5.

**Table 1.5** Na<sup>+</sup> ion conducting composite polymer electrolyte with inactive fillers.

Composite	Ionic Cond. ( $\Omega^{-1}\text{cm}^{-1}$ ) at 40-80°C	Important observations	Reference
PEO-NaNO <sub>3</sub> -8wt% Al <sub>2</sub> O <sub>3</sub>	$1.86 \times 10^{-4}$	ESW ~ 4V	Jinisha et. al. (2017) [47]
PEO <sub>20</sub> -NaClO <sub>4</sub> -5wt% Al <sub>2</sub> O <sub>3</sub>	$2.0 \times 10^{-4}$	ESW ~ 4.58 V	Gao et. al. (2017) [48]
PEO <sub>20</sub> -NaClO <sub>4</sub> -5wt% TiO <sub>2</sub>	$2.62 \times 10^{-4}$	49.2 mAhg <sup>-1</sup> for NCMO/CPEs/Na cell	Nimah et. al. (2015) [29]
PEO <sub>13</sub> -NaClO <sub>4</sub> -3 wt% SiO <sub>2</sub>	$6.4 \times 10^{-4}$	$t_{\text{Na}^+} \sim 0.56$	Wang et. al. (2018) [49]
PEO <sub>20</sub> -NaFSI-3 wt% TiO <sub>2</sub>	$5.0 \times 10^{-4}$	$t_{\text{Na}^+} \sim 0.39$	Zhu et. al. (2019) [50]
PEO <sub>25</sub> -NaClO <sub>4</sub> - 10 wt% SnO <sub>2</sub>	$3.6 \times 10^{-6}$	ESW ~ 3.2	Hashmi et. al. (2000) [51]
PEO <sub>25</sub> -NaI- 10 wt% SnO <sub>2</sub>	$3.5 \times 10^{-6}$	ESW ~ 1.9	Hashmi et. al. (2000) [51]

#### 1.4.2. Composite polymer electrolyte with active fillers

Since the amount and size of the fillers limit the conductivity enhancement in CSPEs, dispersion of ion-conducting (known as active) fillers in CSPEs has been attempted recently.

As compared to the inert fillers, the Li<sup>+</sup>/Na<sup>+</sup> ion FICs as active fillers may more effectively enhance the electrochemical performance of composites solid polymer electrolytes since they can also contribute to the Li<sup>+</sup>/Na<sup>+</sup> ion migration in addition to creating amorphous regions. In general, the Li<sup>+</sup> ion FICs include garnet-type, NASICON-type, perovskite-type, and sulfide-type materials [52]. Some of the reported Li<sup>+</sup> ion FICs are discussed as follows.

**Garnets:** The ideal garnet-type FICs exhibit a general chemical formula of A<sub>3</sub>B<sub>2</sub>(XO<sub>4</sub>)<sub>3</sub> (A = Ca, Mg, Y, La or rare-earth; B = Al, Fe, Ga, Ge, Mn, Ni or V; X = Si, Ge, Al) where A, B, and C are eight, six and four oxygen coordinated cation sites in a crystalline face-center-cubic structure. The Li-rich Li<sub>5</sub>La<sub>3</sub>M<sub>2</sub>O<sub>12</sub> (M = Nb, Ta) were the first reported Li<sup>+</sup> conducting garnets with the ionic conductivity of  $\sim 10^{-6} \Omega^{-1}\text{cm}^{-1}$  at 25°C [53]. Afterward, a series of garnet-type SSEs were discovered. Murugan *et al.* [54] reported the Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) based Li-rich garnet with an ambient ionic conductivity of  $5.11 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ . Some of the reported perovskites are given in Table 1.6.

**NASICON structured Li<sup>+</sup> ion conductors:** These are materials with high ionic conductivity and good structural stability and can be applied in solid-state lithium/sodium metal batteries [23]. The NASICON-type Na<sub>1+x</sub>Zr<sub>2</sub>P<sub>3-x</sub>Si<sub>x</sub>O<sub>12</sub> was reported by Goodenough *et al.* [55] early in 1976. The crystalline framework of NASICON has a 3D network structure with tunnels for Na<sup>+</sup> transport. By substituting Li<sup>+</sup> for Na<sup>+</sup>, NASICON-type materials take the form of Li<sup>+</sup> fast ionic conductors without the change of their original 3D crystal structure. These FICs have a general formula of LiM<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> containing exclusively tetravalent ions M<sup>4+</sup> (M = Ti, Ge, Zr, or Sn). To improve the ionic conductivity of LiM<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, a typical route was adopted by partially replacing tetravalent ions with trivalent ions (M')<sup>3+</sup> (M' = Al, Ge, Ga, Cr, In, Fe, La, *etc.*). Currently most popular NASICON-type FICs are Li<sub>3-2x</sub>(Al<sub>1-x</sub>Ti<sub>x</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) and Li<sub>3-2x</sub>(Al<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) obtained by Al and Ge substitution, respectively, due to their high bulk ionic conductivities in the range of  $10^{-4} \sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$  at room temperature [56]. Some of the reported NASICON structured FICs are given in Table 1.6.

**Perovskite-type ceramics:** These materials have a general formula of ABO<sub>3</sub> (A = La, Sr, or Ca; B = Al or Ti) with cubic unit cell and space group Pm/3m [37]. The typical cubic perovskite structure follows a Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub> (LLTO) formula, where Li<sup>+</sup> ion and La<sup>3+</sup> ion are located at

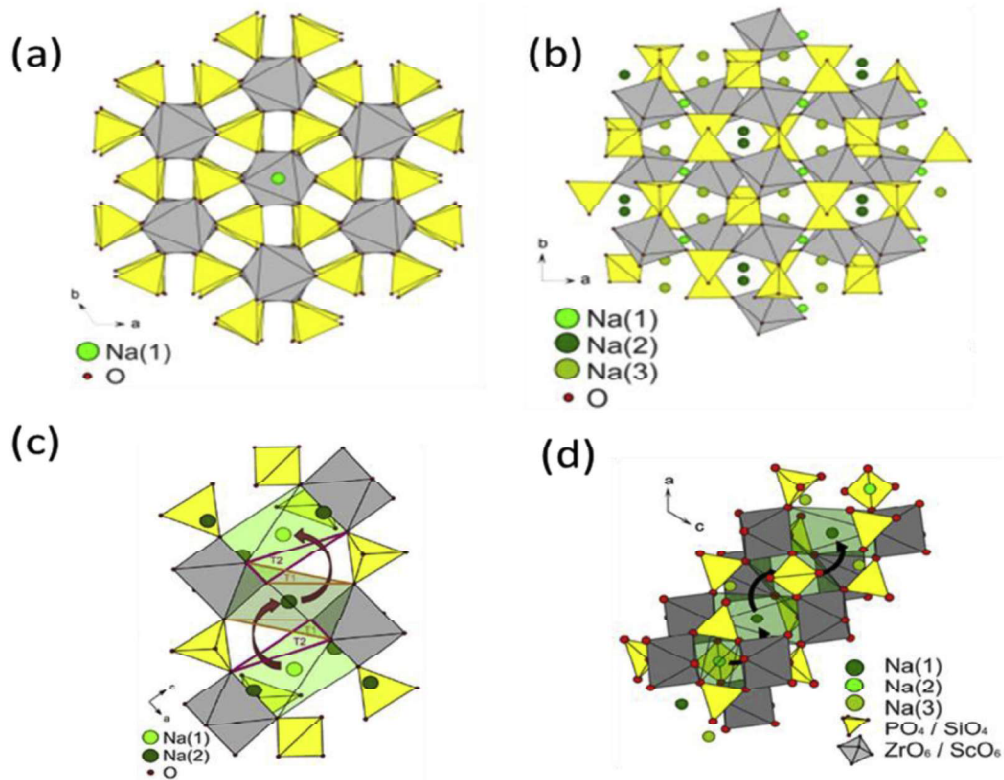
the center of the cube (A sites,) and Ti atoms, octahedrally coordinated with oxygen atoms, occupy the corner of the cube (B sites). The Li<sup>+</sup> ion acts as mobile ions and the La<sup>3+</sup> ion stabilizes the structure [52]. The Li<sup>+</sup> ion migrates along with A-site vacancies and through bottlenecks comprising four oxygen adjacent ions. Some of the reported perovskites are given in Table 1.6.

**Table 1.6.** Li<sup>+</sup>/Na<sup>+</sup> ion conducting fast ionic conductors.

Fast ionic conductor	Structured	Ionic Cond. ( $\Omega^{-1}\text{cm}^{-1}$ ) at RT	Reference
LiTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	NASICON	3.83 x 10 <sup>-7</sup>	Martinez Juarez et. al. (1998) [57]
Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	NASICON	3 x 10 <sup>-3</sup>	Monchak et. al. (2016) [38]
Li <sub>1.2</sub> Ti <sub>1.8</sub> Sc <sub>0.2</sub> (PO <sub>4</sub> ) <sub>3</sub>	NASICON	2.5 x 10 <sup>-3</sup>	Kahlaoui et. al. (2017) [58]
Li <sub>1.6</sub> Al <sub>0.6</sub> Ge <sub>0.8</sub> (PO <sub>4</sub> ) <sub>3</sub>	NASICON	0.7 x 10 <sup>-3</sup>	Maldonado-Manso et. al. (2003) [59]
Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	NASICON	6.20 x 10 <sup>-3</sup>	Parez-Estebanez et. al. (2014) [36]
La <sub>0.57</sub> Li <sub>0.29</sub> TiO <sub>3</sub>	Perovskite	1.60 x 10 <sup>-3</sup>	Inaguma et. al. (2013) [37]
Li <sub>0.35</sub> La <sub>0.51</sub> TiO <sub>2.93</sub>	Perovskite	1.78 x 10 <sup>-5</sup>	Zheng et. al. (2017) [60]
Li <sub>0.35</sub> La <sub>0.55</sub> TiO <sub>3</sub>	Perovskite	9.01 x 10 <sup>-6</sup>	Zhang et. al. (2019) [61]
Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub>	Garnet	1.63 x 10 <sup>-6</sup>	Awaka et. al. (2009) [62]
Li <sub>6.4</sub> La <sub>3</sub> Zr <sub>1.4</sub> Ta <sub>0.6</sub> O <sub>12</sub>	Garnet	1 x 10 <sup>-3</sup>	Hong et. al. (1978) [35]
Li <sub>6.6</sub> La <sub>3</sub> Zr <sub>1.6</sub> Sb <sub>0.4</sub> O <sub>12</sub>	Garnet	7.70 x 10 <sup>-4</sup>	Ramakumar et. al (2013) [63]
Li <sub>6.75</sub> La <sub>3</sub> Zr <sub>1.75</sub> Ta <sub>0.25</sub> O <sub>12</sub>	Garnet	2.4 x 10 <sup>-6</sup>	Reddy et. al. (2017) [64]
Na <sub>3.1</sub> Zr <sub>1.95</sub> Mg <sub>0.5</sub> Si <sub>2</sub> PO <sub>12</sub>	NASICON	3.5 x 10 <sup>-3</sup>	Song et. al. (2016) [65]

$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	NASICON	$6.70 \times 10^{-4}$	Ignaszak et. al. (2005) [66]
$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	NASICON	$1 \times 10^{-3}$	Park et. al. (2016) [67]
$\text{Na}_3\text{Zr}_{1.8}\text{Ge}_{0.2}\text{Si}_2\text{PO}_{12}$	NASICON	$8 \times 10^{-3}$	Park et. al. (2018) [68]
$\text{Na}_{3.4}\text{Zr}_{1.8}\text{Zn}_{0.2}\text{Si}_2\text{PO}_{12}$	NASICON	$8.05 \times 10^{-4}$	Jolley et. al. (2015) [69]

Among the FICs, NASICON framework materials were chosen for composites preparation. Thus a brief discussion on NASICON structure was discussed in this section. The NASICON framework is originated from the  $\text{NaM}_2(\text{PO}_4)$  ( $\text{M} = \text{Ge}, \text{Ti}, \text{or Zr}$ ), generally with a rhombohedral unit cell (space group  $R\bar{3}c$ ) [70], which consists of corner-sharing  $\text{PO}_4$  tetrahedra and  $\text{MO}_6$  octahedra (Fig. 1.3).



**Figure 1.3** NASICON-type (a) rhombohedral ( $R\bar{3}c$ ) structure and (b) monoclinic ( $C2/c$ ) structure (the yellow tetrahedra and the grey octahedra correspond to  $\text{SiO}_4/\text{PO}_4$  and  $\text{ZrO}_6$  units, respectively); Na ion conduction pathway in NASICON-type (c) rhombohedral and (d) monoclinic structure (after Guin et al [74]).

Two  $\text{MO}_6$  octahedra and three  $\text{PO}_4$  tetrahedra share oxygen atoms and create the so-called lantern units [71][72], which are assembled to form a 3D network structure. Interestingly, when Na atoms are replaced by Li, the material maintains its NASICON structure and turns into Li-ion conductor with high conductivity. There are three different sites in the structure for cations [73][74]: M1 sites (Li1, 6-fold oxygen coordination), M2 sites (Li2, 10-fold oxygen coordination), and M3 sites (Li3, between M1 and M2, 4-fold oxygen coordination). For small tetravalent cations like Ge and Ti,  $\text{LiGe}_2(\text{PO}_4)_3$  (LGP) and  $\text{LiTi}_2(\text{PO}_4)_3$  (LTP) maintain rhombohedral phase, M1 sites are preferentially occupied by Li-ions. For larger tetravalent cations like Zr, Sn, Ga and Hf,  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{LiSn}_2(\text{PO}_4)_3$ , and  $\text{LiHf}_2(\text{PO}_4)_3$  deteriorate to a triclinic phase at low temperatures (about under 300 K) and Li-ions are moved to M3 sites [75]. All these sites are arranged in an alternating way along conducting channels. The ionic conduction takes place through ion hopping from M2 sites to M3 sites.

In recent years, enormous efforts have been made to develop high-performance composites polymer electrolytes (CPEs) by integrating polymer electrolytes with  $\text{Li}^+$  ion conducting garnet type fillers (such as  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ,  $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ ,  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ ,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ,  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ , and lithium montmorillonite) [76]. These CPEs demonstrate multiple advantages inherited from fillers and polymer matrices, particularly high ionic conductivity at room temperature, superior electrochemical and thermal stability, non-flammability, and interfacial compatibility with electrodes. Since Garnet-structured electrolytes are chemically inert against lithium metal, these were considered as promising reinforcers in polymer composites electrolytes. Li et al. [76] reported polymer nanocomposite of PVDF-HFP with different amounts of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) nanofibers and explored the effect of the filler content on the ionic conductivity. A maximum ionic conductivity of  $9.5 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  with 10 wt % LLZO filler was reported, which was approximately one order of magnitude higher than that of the pure PVDF-HFP/Li salt electrolyte.

Similar to polymer-garnet composites, significant influence on ionic conductivity has been observed when perovskite fillers were incorporated into the polymer matrices in the form of particles. In addition to the effect of particle size, the shape of perovskite fillers influences greatly the  $\text{Li}^+$ -ion conduction. Liu et al. [77] reported the impacts of  $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$  (LLTO)

nanowires with LLTO nanoparticles on the ionic conductivity improvement of PAN//LLTO/LiClO<sub>4</sub> composite electrolytes. The nanowire-filled electrolyte showed ~ 10 times higher conductivity than that of the nanoparticles-filled composite. Similarly, Bae et al. [78] developed a 3D Li<sub>0.35</sub>La<sub>0.55</sub>TiO<sub>3</sub> framework as a nanostructured filler for the composite solid electrolyte. The interconnected LLTO framework not only offered continuous long-range Li<sup>+</sup> ion pathways but also greatly enhanced the mechanical strength of the composite electrolyte.

Among the NASICON type ceramic electrolyte, Li<sub>1+x</sub>Al<sub>x</sub>Ti<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) and Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) are the most successful ones [79]. Both of these materials have been widely studied. An optimized composition could provide an ionic conductivity of  $1.7 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  at room temperature. In an interesting work, Wang et al. [80] reported the incorporation of active filler LATP with enhanced ionic conductivity. A maximum ionic conductivity of  $1.70 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  at 20°C was reported for 10 wt% LATP with ~ 65 nm size nanoparticles. Recently, Liu et al. [81] also prepared PEO-LATP-LiTFSI composite polymer electrolyte films with a maximum ionic conductivity of  $1.2 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$  at 30°C for the composite with 1 wt% of LATP. Table 1.7 summarized some of the reported Li<sup>+</sup> ion conducting composites polymer electrolytes.

**Table 1.7** Composite polymer electrolyte with Li<sup>+</sup> ion conducting active fillers.

Composite	Ionic conductivity ( $\Omega^{-1}\text{cm}^{-1}$ )	Important observation	Reference
PEO <sub>18</sub> -LiTFSI-1 wt% Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>	$1.21 \times 10^{-3}$ (80°C)	ESW ~ 5 V $t_{\text{Li}^+} \sim 0.26$	Zhao et. al. (2016) [82]
P(EO) <sub>18</sub> -LiTFSI- 20 wt% Li <sub>1.5</sub> Al <sub>0.5</sub> Ge <sub>1.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	$6.76 \times 10^{-4}$ (60°C)	ESW ~ 5 V	Zhao et. al. (2016) [83]
PEO-LiTFSI-10 wt% Li <sub>6.4</sub> La <sub>3</sub> Zr <sub>1.4</sub> Ta <sub>0.6</sub> O <sub>12</sub>	$1.17 \times 10^{-4}$ (30°C)	ESW ~ 5 V	Chen et. al. (2018) [84]
PEO-LiTFSI- Li <sub>0.3</sub> La <sub>0.557</sub> TiO <sub>3</sub>	$1.8 \times 10^{-4}$ (30°C)	ESW ~ 4.5 $t_{\text{Li}^+} \sim 0.33$	Wang et. al. (2019) [85]

PEO-LiClO <sub>4</sub> - 10wt % Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	$1.7 \times 10^{-4}$ (20°C)	Huge conductivity enhancement	Wang et.al. (2017) [80]
PEO-LiClO <sub>4</sub> - 50wt % Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	$1.6 \times 10^{-3}$ (80°C)	ESW ~ 4.6V $t_{Li^+} \sim 0.216$	Ban et. al. (2018) [86]
PEO <sub>8</sub> -LiTFSI-26	$1.67 \times 10^{-4}$ (27°C)	ESW ~ 4.5V	Wang et. al. (2019) [87]
PEO <sub>16</sub> -LiTFSI- Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub>	$2.3 \times 10^{-4}$ (27°C)	ESW ~ 4.5V	Wan et. al. (2017) [88]
5LiCF <sub>3</sub> SO <sub>3</sub> - 95[PEO <sub>0.1</sub> LTP <sub>0.9</sub> ]	$7 \times 10^{-4}$ (27°C)	Huge conductivity enhancement	Singh et. al. (2017) [89]
5LiCF <sub>3</sub> SO <sub>3</sub> -95[PEO <sub>0.3</sub> LATP <sub>0.7</sub> ]	$10^{-4}$ (45°C)	$t_{Li^+} \sim 0.46$	Singh et. al. (2020) [90]

Similar to Li<sup>+</sup> ion conducting CPEs, several studies have been carried out to developed Na<sup>+</sup> ion conducting CPEs, in which fast ion-conducting fillers have been added in place of insulating particles. Plocharski et. al. [91] have studied the dispersion of superionic Na<sup>+</sup> ion conducting NASICON crystallites (NTP) in PEO-NaI based SPEs. They reported an enhancement in the ionic conductivity by nearly one order of magnitude in comparison to the host matrix. Zhang et al. [92] developed solvent-free PEO-based CSPEs with two different sodium superionic conductors (NASICON) as inorganic fillers (i.e., Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> and Na<sub>3.4</sub>Zr<sub>1.8</sub>Mg<sub>0.2</sub>Si<sub>2</sub>PO<sub>12</sub>) for sodium batteries. The ionic conductivities of CPEs were enhanced after adding NASICON-type fillers into the electrolytes due to (i) the introduction of fillers decreased the crystallization degree and improved the Na<sup>+</sup> transport in the amorphous region; and (ii) the percolation effect which was able to form continuous and interconnected Na<sup>+</sup> transport paths on the surface of the NASICON particles; and (iii) the transport of Na<sup>+</sup> ions in the NASICON bulk contributed to the overall conductivity of the as-prepared CSPE [92]. Manthiram et al. [93] also reported a solid-state sodium cell assembled with the Na<sub>2</sub>MnFe(CN)<sub>6</sub> cathode and NaClO<sub>4</sub>/PEO/Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> electrolyte, which exhibited a stable cycling performance as compared to the cells with the pristine NaClO<sub>4</sub>/PEO electrolyte. A superior behavior of the CSPEs-based cells was attributed to the presence of Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> nano filler that increased the mechanical stability of the electrolyte and retarded the growth of



Na<sup>+</sup> dendrites during cycling. In addition, Ciucci et al. [94] also demonstrated that CSPEs comprising of NaClO<sub>4</sub>, polyvinylidene fluoride (PVDF), and Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> could not only suppress the growth of Na<sup>+</sup> dendrites but also effectively impede the dissolution and migration of Mn<sup>4+</sup> ions from the Na<sub>0.67</sub>MnO<sub>2</sub> cathode, enabling good cycling stability and rate performance of the cells. Some of the recently reported composites along with their ionic conductivity are illustrated in Table 1.8.

**Table 1.8** Some of the recent Na<sup>+</sup> ion-conducting composite solid polymer electrolytes with active fillers.

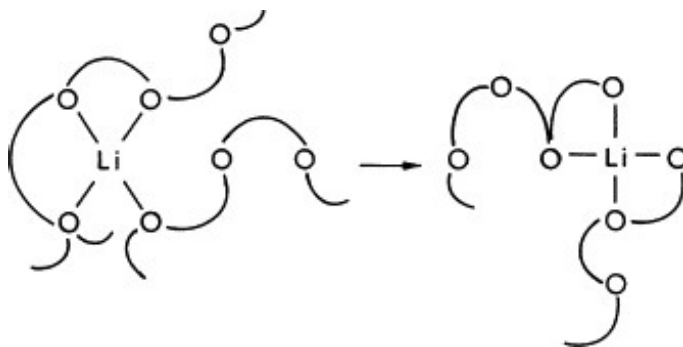
Composite	Ionic cond. ( $\Omega^{-1}\text{cm}^{-1}$ ) at 60-80 °C	Important observations	Reference
PEO <sub>12</sub> -NaFSI- 40 wt% Na <sub>3.4</sub> Zr <sub>1.8</sub> Mg <sub>0.2</sub> Si <sub>2</sub> PO <sub>12</sub>	$2.4 \times 10^{-3}$	ESW ~ 4.7V, capacity ~ 106.1 mAhg <sup>-1</sup> with appreciable charge retentivity	Zhang et. al. (2016) [95]
PEO <sub>12</sub> -NaTFSI-50 wt% Na <sub>3.4</sub> Zr <sub>1.8</sub> Mg <sub>0.2</sub> Si <sub>2</sub> PO <sub>12</sub>	$2.8 \times 10^{-3}$	ESW ~ 4.3V, capacity ~ 107 mAhg <sup>-1</sup>	Zhang et. al. (2017) [96]
PEO <sub>15</sub> -NaClO <sub>4</sub> - 25 wt% Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub>	$5.6 \times 10^{-4}$	capacity ~ 109.3 mAhg <sup>-1</sup> with excellent charge retentivity	Yu et. al. (2019) [93]
10 NaI- 90[PEO <sub>0.3</sub> NTP <sub>0.7</sub> ]	$4 \times 10^{-5}$	Conductivity-structure correlation	Singh et. al. [97]
10 NaCF <sub>3</sub> SO <sub>3</sub> - 90[PEO <sub>0.3</sub> NTP <sub>0.7</sub> ]	$3 \times 10^{-5}$	Electrolyte stability window of 3 V	Singh et. al. [98]
63NZSP- 37(PEO <sub>0.87</sub> NaI <sub>0.13</sub> )	$10^{-4}$	ESW ~ 4.64 V vs Na/Na <sup>+</sup>	Singh et. al. [99]

## 1.5. Ion transport mechanism in solid electrolyte

### 1.5.1. Polymer electrolytes

Ever since the advent of SPEs, researchers have shown keen interest in investigating an in-depth understanding of the ion transport mechanism. Importantly, the polymer matrix should

first have the ability to dissolve  $\text{Li}^+/\text{Na}^+$  salts, and then form a complex. The ideal system is composed of a  $\text{Li}^+/\text{Na}^+$  salt and a polymer with a high dielectric constant, which can ensure complete dissociation of the salt and the transmission of ions. The polymer electrolyte possessing polar groups such as  $-\text{O}-$ ,  $-\text{C}=\text{O}$ ,  $-\text{S}-$ ,  $-\text{CN}-$ ,  $-\text{P}-$  and other functional groups can effectively dissolve alkali metal salts to form polymer- $\text{Li}^+/\text{Na}^+$  salt complexes. It is usually recognized that in SPEs, the ionic conductivity is proportional to the concentration of free ions and the number of ion migrations. The transmission of  $\text{Li}^+/\text{Na}^+$  (cations) mainly depends on the segment motion within the amorphous region in the polymer electrolyte. The polymers with lower  $T_g$  have greater flexibility of the polymer chains, which can facilitate segment movement [100]. The conduction mechanism of cations ( $\text{Li}^+/\text{Na}^+$ ) in the polymer electrolyte is shown in Fig. 1.4.



**Figure 1.4.** Ion chain coupling relaxation in polymer-salt system (after Stephan et. al. [101]).

The  $\text{Li}^+$  ions coordinate with the polar group on the polymer segment [102–104] (e.g.,  $-\text{O}-$  in polyethylene oxide (PEO) that is driven by the electric field, cations undergo complexation/dissociation with the polymer segment and migrates from a coordination site to a new site in the neighborhood [102][103]. At high temperatures, the polymer produces free volume through increased local segment motion [104], cations jump from one polymer chain to another, thereby contributes to electrical transport in a direction to which electric field is applied [104].

Several interesting studies have shown that the relationship between ion conductivity and temperature in the SPEs follows two main conduction mechanisms [105] viz. the Vogel-Tamman-Fulcher (VTF) model and the Arrhenius model. The Vogel-Tamman-Fulcher (VTF) model can be expressed by relation (1):

$$\sigma(T) = AT^{-1/2} \sigma_0 \exp \frac{B}{K_B(T-T_0)} \dots\dots\dots (1)$$

From Eq. (1):  $\sigma_0$  is the frequency factor, which is related to the number of charge carriers; B is the activation energy of ion conduction; T is the operating temperature;  $T_0$  is the equilibrium glass transition temperature ( $T_0 = T_g - 50K$ );  $T_g$  is the glass transition temperature. The VTF formula [105] was first proposed to explain the diffusion process in glassy and disordered materials, which was derived from quasi-thermodynamic theory, emphasizing free volume changes and coordination entropy. For polymer electrolytes, the relationship curve between  $\sigma$  and  $1/T$  is usually non-linear, which indicates that the mechanism of conductivity involves ion hopping motion and relaxation/breathing or segment motion of the polymer chain [106]. The current VTF formula is often used to describe the ion transport behavior of polymer solid electrolytes above the glass transition temperature, gel polymer electrolytes, organic liquid electrolytes, and ionic liquids [107]. Moreover, the Arrhenius equation can be expressed by Eq. (2):

$$\sigma_{dc}(T) = \sigma_0 \exp \frac{E_a}{K_B T} \dots\dots\dots (2)$$

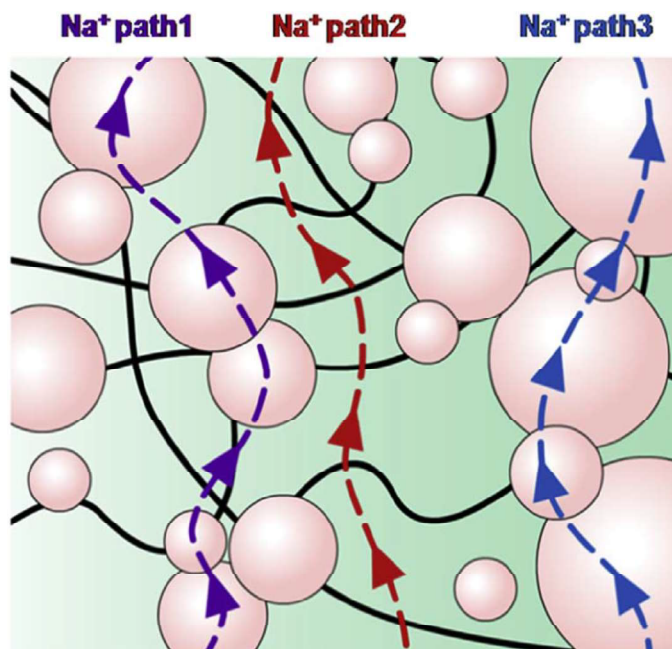
In Eq. (2):  $K_B$  is the Boltzmann's constant, and other parameters are as described in Eq. (1). Arrhenius behavior is usually related to the ion hopping motion that accompanies the long-range motion in the matrix [108][109]. The ion transport occurs through a simple hopping mechanism without ion-chain coupling.

### 1.5.2. Polymer-fillers composites

The ion conduction is rather complex in ceramic-polymer composite electrolytes. Compared with the ceramic-free polymer electrolytes, the ion movement could be further facilitated in the polymer host with the addition of ceramic fillers, due to the reduced crystallinity of the polymer host [39][40][79]. Additionally, the mobile ions are also likely to transport within the introduced active ceramic fillers and the ceramic-polymer interfaces, both of which provide even faster conduction pathways over the polymer matrix [88][95]. It is found that the composite's conductivity is strongly dependent on the amount of the added ceramic fillers [29] [96].

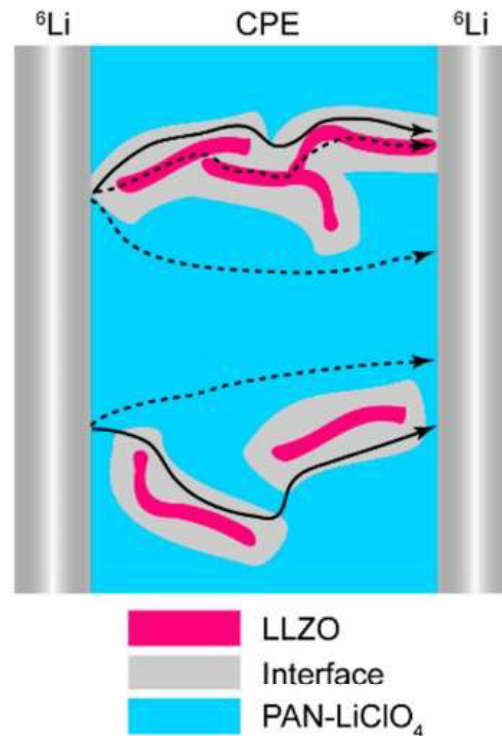
According to the effective medium theory model [110][111], the composite's conductivity would continuously increase with the amount of the ceramic fillers, if the ceramic fillers could

form into percolation clusters (with continuous ceramic-polymer interface). However, in most cases, the conductivity decreases after reaching a certain amount of ceramic fillers, because of the aggressive agglomeration of the ceramic particles (inactive fillers) [41][42]. On the contrary, greatly enhanced ionic conductivity has also been achieved in ceramic-polymer composites with a higher degree of percolation (active fillers) [86][96]. Zhang et. al.[96], proposed a possible qualitative ion transport mechanism in the presence of ceramic fillers (illustrated in Fig. 1.5); (a) the addition of NASICON ceramic fillers suppresses the degree of crystallization and enhances the segmental motion of the polymer matrix, thus not only enlarges the ion-conducting region, but also enhances the carrier mobility; (b) the percolation effect may also play an important role in the conductivity enhancement which arises from the formation of high degree of continuous and interconnected transport channels on the surface of the NASICON particles; (c) owing to the concentration gradient between the high conductive NASICON particle, the  $\text{Na}^+$  in NASICON can be absorbed by the polymer matrix considering that PEO provides a high degree of dilution of salt, which increases the  $\text{Na}^+$  ion vacancies on the surface of NASICON crystallites and facilitates the ion transport along the surface regions; and (d) the highly conductivity of the NASICON ceramic bulk is also beneficial to increase the total conductivity of the CPE membranes.



**Figure 1.5** Schematic illustration of  $\text{Na}^+$  ion transport in composites polymer electrolytes (after Zhang et. al. [96]).

Similarly, Yang et. al. [112] suggest  $\text{Li}^+$  ion transport pathways in composites polymer electrolytes as through (i) polymer phase, (ii) LLZO nano wire phase and (iii) interface region between the polymer and LLZO. The schematic of  $\text{Li}^+$  ion pathways is shown in Fig. 1.6.

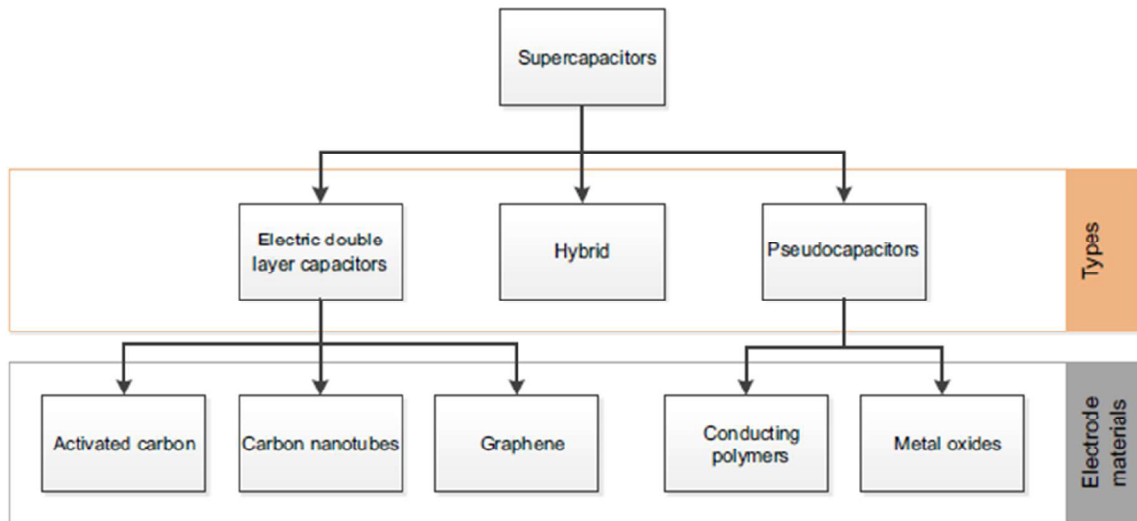


**Figure 1.6** Schematic showing possible  $\text{Li}^+$  transport pathways in the CPE (after Yang et. al [112]).

## 1.6. Supercapacitors (SCs)

### 1.6.1. General Introduction:

With the growing demand for EVs and portable device systems, e.g. hybrid electric vehicles, memory backup and portable devices, the need of suitable energy storage devices is realized that can additionally provide high power density and rapid charging-discharging for large number of cycles. A supercapacitor (SC) is a promising passive electrostatic charge storage device that exhibits high power density, fast discharging-charging for a relatively long lifetime. Broadly SCs can be categorized into (i) electrochemical double-layer capacitors (EDLCs), where the energy is stored through adsorption of ions at the interface of the electrode, (ii) pseudocapacitors, which store energy through redox reaction [113] and, (iii) hybrids capacitors that are fabricated combining EDLC and pseudo mechanism. Different types of supercapacitors according to mechanism of energy storage are classified in Fig. 1.7.

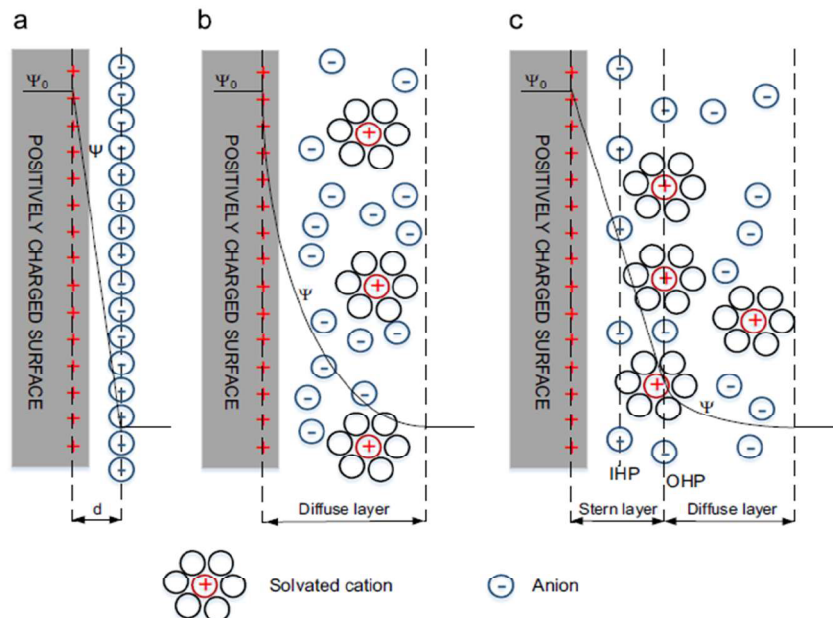


**Figure 1.7** Classification of different supercapacitors (SCs) (after Gonzalez et. al. [115]).

EDLCs are based on high specific-surface area nanoporous materials as active electrode materials, leading to a huge capacitance in comparison with electrostatic capacitors. The electrodes are usually made of nanoporous carbon materials. Pseudo capacitors are based on conducting polymer or metal oxide-based electrodes [114], and sometimes functionalized porous carbons, combining electrostatic and pseudocapacitive charge storage mechanisms. These materials can hold much higher specific capacitance values as compared to EDLCs, with the charge storage mechanism relying on fast redox reactions occurring on the electrode surface but not in the bulk like in batteries. However, like in the case of batteries, redox reactions can lead to mechanical changes making the electrodes swell and shrink, giving rise to poor mechanical stability. Consequently, lower cycle life is an important deficiency of pseudo capacitive materials. Finally, hybrid capacitors are composed of an EDLC electrode and a pseudo capacitive or battery type electrode, combining the properties of both systems and leading to an intermediate performance in some cases.

Stern model suggested a satisfactory description of the formation of electric double layer in EDLCs. The model summarized the combination of both Helmholtz and Gouy-Chapman model as shown in Fig. 1.8. As suggested by the electric double layer model, when a supercapacitor is charged, cations within the electrolyte concentrate near in one electrode and anions near another electrode forming an EDL (shown in Fig. 1.8c) that compensates the

external charge unbalance. During the discharge, electrons travel from the negative electrode to the positive electrode through an external circuit, and simultaneously ions at the interface forming EDL again travel back to the electrolyte until the cell is discharged.



**Figure 1.8** EDL models, (a) Helmholtz model, (b) Gouy–Chapman model, and (c) Stern model (after González *et. al.* [115]).

Pseudo capacitance is essentially due to a Faradaic charge storage mechanism based on fast and highly reversible surface or near-surface redox reactions [114]. These processes occurring at the interface enhance the energy content and also increase the charge storage ability. Nevertheless, it is also a fact that pseudocapacitors exhibit a relatively low power density and poor cycling stability when compared with EDLCs. Generally, redox-active materials are used as electrodes. When an external potential is applied, reversible and fast redox reactions occur on the electrode. This is governed by the passage of charge between electrolyte and electrode. Materials used for building such electrodes are normally carbons, metal oxides, and conducting polymers [116]. Electrodes exhibiting pseudo capacitance are more prone to swelling and shrinking on charge/discharge cycling, which can lead to poor mechanical stability and low cycle life [117]. The mechanism of charge and discharge of a pseudocapacitor is similar to the one of the batteries.

### 1.6.2. Electrodes:

The energy density of an SC is largely considered an electrode property. Therefore, materials having high surface area and uniform porosity distribution have been widely explored for electrode applications for EDLCs in recent years [114] [118]. These materials such as activated carbon [114], porous carbon [118], carbon aerogels [118], carbon nanotubes (CNTs) [119] etc. having high surface area, regular porous distribution, high conductivity have been reported as efficient and potential electrode materials for EDLC applications. Some of the reported activated carbon along with their surface area is shown in Table. 1.9.

**Table 1.9.** BET specific surface areas ( $S_{bet}$ ) for different carbon precursors *after* González *et al.* [115].

Carbon precursor	Activation method	$S_{bet}$ ( $m^2-g^{-1}$ )
Coconut shell	KOH	1060
Eucalyptus wood	KOH	2970
Firewood	steam	1130
Bamboo	KOH	1290
Cellulose	KOH	2460
Sucrose	CO <sub>2</sub>	2100
Banana fiber	ZnCl <sub>2</sub>	1100
Apricot shell	NaOH	2335
Wheat straw	KOH	2316
Rice husk	KOH	1390
Rice husk	NaOH	1890

In case of Pseudo capacitors, metal oxides were generally used for electrode fabrication as they lead to high energy and high power densities [120]. There are different metal oxide materials used for electrode fabrication such as RuO<sub>2</sub> [121], IrO<sub>2</sub> [122], MnO<sub>2</sub> [123], NiO [124], Co<sub>2</sub>O<sub>3</sub> [125], V<sub>2</sub>O<sub>5</sub> [126]. The most studied ones are ruthenium and manganese oxides [8]. These oxides have a high potential window, good thermal stability, high rate capability, and high



reversible redox reaction. Ruthenium undergoes highly reversible redox reaction viz. oxidation to  $\text{RuO}_4^{2-}$ ,  $\text{RuO}_4^-$ ,  $\text{RuO}_4$  on charging and reduced back to  $\text{RuO}_2$  on discharging [121].

### 1.6.3. Gel/Liquid electrolytes in supercapacitors:

The majority of the SCs in the market use a liquid electrolyte [127] in which salts e.g. tetraethylammonium tetrafluoroborate ( $\text{TEABF}_4$ ) or lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ) are dissolved in solvents of the type propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DME) or ethylene carbonate (EC). In the last few decades, SCs have also been developed using polymer gels as separators [128] [129]. A separator (electrolyte) plays an important role as a charge transport medium between electrodes. Gel polymers as electrolyte not only provide high ionic conductivity but also relatively better operating voltage that in turn improves the energy density and power density of SCs. Thus, the focus has been on novel electrolyte materials with high ionic conductivity and ECS window. Organic polymer such as poly (ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), porous poly(vinylidene fluoride) (PVdF) etc have been used as a matrix in these GPEs have been widely studied in their gel electrolyte/separator form for developing supercapacitors. For example, Tiruye et. al. [128] have reported a supercapacitor with high electrochemical stability window up to 3.5V with ionic liquid based polymer as electrolyte and activated carbon as electrode. Similarly, Chaudoy et. al. [129] have also reported quasi-solid state supercapacitor using gel polymer electrolyte via incorporation of a room temperature ionic liquid into a cross-linked polymer matrix. The authors reported a specific energy of  $16 \text{ Wh Kg}^{-1}$  at  $1.1 \text{ kW kg}^{-1}$  and a columbic efficiency of 99.9%. Bon et. al. [130] have reported poly(vinyl alcohol) (PVA)-ceramic composite (PVACC) as separators with aq. KOH as electrolyte for supercapacitor applications leads to 14.4% higher specific capacitance than those with bare PVA separator. Similar studies have also been reported for gel polymer embedded with ceramic nanofillers ( $\text{Al}_2\text{O}_3$ ) as an efficient electrolyte for SC applications [131]. In an interesting work by Subramaniam et. al. [132], a flexible solid-state supercapacitor with high energy density ( $\sim 50 \text{ Wh Kg}^{-1}$ ) and power density of ( $4400 \text{ W Kg}^{-1}$ ) have been reported using single-wall CNT as electrode.

#### 1.6.4. Solid electrolyte in a supercapacitor:

Similar to  $\text{Li}^+$  ion batteries, the SC electrolytes also required high ionic conductivity and electrochemical stability window. Use of liquid or gels limits flexibility, thermal stability [133]. In addition, safety concerns about flammability have also drawn attention due to which interest is now shifted towards all-solid-state supercapacitors (ASSCs) [133]. To overcome issues pertaining to liquids/gels, various groups have carried out studies to develop highly conducting flexible solid electrolytes. In an interesting work, Wang et. al. [134] have developed a thermally stable solid polymer electrolyte with a poly (aryl ether ketone)–poly(ethylene glycol) copolymer as a polymer host, and  $\text{LiClO}_4$  as electrolyte and reported specific capacitance of  $103.17 \text{ F g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  with activated carbon electrodes. Lee et. al. [135] have reported a flexible solid-state supercapacitor with a specific capacitance of  $239.3 \text{ F-g}^{-1}$  based on an amphiphilic comb polymer (CP) (PAEK-PEG- $\text{LiClO}_4$ ) with  $\sim 10^{-4} \Omega^{-1}\text{cm}^{-1}$  at  $30^\circ\text{C}$  as solid electrolyte and an electrode based on porous one-dimensional hierarchical carbon nanotubes.

On the other hand, with such a rise in the demand for energy storage devices, it has been realized that the possible depletion of lithium in nature may limit the cost-effectiveness of  $\text{Li}^+$  ion devices. Thus, alternative energy storage devices with  $\text{Na}^+$  ion conducting energy materials having similar chemistry have very recently attracted the scientific community [136]. This is also because of the abundance of sodium resources on a global scale. Similar to  $\text{Li}^+$  ion-based batteries,  $\text{Na}^+$  ion-based devices also use organic electrolytes, because of their similar advantages e.g. high  $\text{Na}^+$ -ion conductivity and facile wettability [93]. Thus, in the recent few years,  $\text{Na}^+$  ions conducting gel and solid electrolytes have also got emphasis. Use in ASSBs is already being explored by many groups [86][96] [112]. However, the use of these solids-state  $\text{Na}^+$  ion conducting electrolytes still needs to be explored for all-solid-state supercapacitors.

From the above literature survey, it may be concluded that:

- (a) Vigorous interesting investigations have been carried out in the last two decades to developed highly ion-conducting composite polymer electrolytes using active and inactive ceramic fillers (active and inactive). Interestingly, the ionic conductivity of the order of  $10^{-5}$ - $10^{-4} \Omega^{-1}\text{cm}^{-1}$  at the ambient temperature has been achieved for  $\text{Li}^+$  ion-conducting systems.

- .....
- (b) Polymer composites with fast ionic conductors Viz. NASICON, Garnet, Perovskites etc. have gathered a considerable interest because of their 3D networks pathways for cation movement. Also, due to ion conducting nature of these materials, composites with them using active fillers has got wide spread attention over the inactive or insulating fillers.
  - (c) Due to scarcity of the lithium resources, an alternative to  $\text{Li}^+$  ion-conducting systems has got attention in the last few decades.  $\text{Na}^+$  ion-based SPEs dispersed with active fillers have been reported in the last few years.
  - (d) Attention has also been on the application of various NASICON analogues (e.g. LAGP, LATP, LAZTP etc.) as dispersoids/fillers in the polymer matrix.
  - (e) There is though little but important work on the use of active filler-based polymers in  $\text{Li}^+$  ion batteries.

### 1.7. Gaps in the existing research

Even though several groups have attempted to improve the ionic conductivity of the polymer composite by different approaches, the conductivity of the SPE further needs improvement for applications in  $\text{Li}^+$  and  $\text{Na}^+$  ion-based solid ionic devices. The following issues need to be addressed.

1. With the dispersion of insulating nanofillers, the ionic conductivity improves up to a certain extent. However, the rise is limited due to the size and content of fillers. Thus, to further improve the ionic conductivity, it is important to explore an alternative of these fillers that do not restrict the ionic motion but provide pathways for ionic transport. Very recently introduced active filler-based polymer composites possibly have potential. However, a systematic study of their electrical, structural, thermal properties is still required. A mechanism of electrical transport in active filler-based composites is required.
2. There are some SPEs developed with high ionic conductivity but such systems lack thermal and electrochemical stability. It is inevitable therefore to explore new generation composites based on polymer hosts that can provide flexibility in a wider composition, thermal and electrochemical stability.

3. Active fillers in polymers have recently got attention, but polymer in active filler can be another approach to obtain high conductivity. Very little work is available in the literature on the mechanism of conductivity. Particularly, when NASICON content is high, there is no consensus about cation pathways. The role of active filler grains in enhancing conductivity still requires better understanding via conductivity-structure correlation studies.
4. Important advanced techniques for structure investigations have not been fully explored in the field of polymer electrolytes. For example, XAS (soft X-ray absorption spectroscopy), XANES (X-ray absorption near-edge spectroscopy), XPS (X-ray photoelectron spectroscopy) are some of the sophisticated characterization techniques which can lead to a better understanding of the structure and its relation with electrical transport.
5. The application of these composites in ASSBs has been recently examined by various groups. Their possible use in supercapacitors as an electrolyte has not been explored so far. Quite less emphasis has been given on SPE-based supercapacitors. Thus, ASSC device fabrication and testing require attention.
6. In addition, the mechanism of high capacitance, the role of the high ionic conductivity of the solid electrolyte, and issues related to in solid-solid interface lack clarity.

### 1.8. Statement of the problem and objectives:

Solid polymer electrolytes (SPEs) have several advantages over traditional organic liquid-based electrolytes. However, due to low ionic conductivity, these could not be commercially applied so far in all-solid-state battery applications. Various approaches have been adopted to enhance the ionic transport in SPEs, e.g. use of plasticizers, fine insulating particles as fillers in the polymer matrix. These attempts though were able to enhance conductivity appreciably; its value is still not adequate for device applications. For conductivity value close to those of liquid electrolytes, a search of  $\text{Li}^+$  and  $\text{Na}^+$  ion-based hybrid polymer composites could be an alternative approach.

Present work plans to (i) develop polymer hybrids dispersed with  $\text{Li}^+/\text{Na}^+$  NASICON nanoparticles in large and small amounts, (ii) attempts to propose a more generalized mechanism of electrical transport by correlating the structure with electrical properties, and

(iii) explores the application of these developed hybrid polymer-NASICON electrolytes in all-solid-state  $\text{Na}^+$  and  $\text{Li}^+$  ion supercapacitors.

### Objectives

- i) Synthesis of  $\text{Li}^+$  and  $\text{Na}^+$  ion conducting novel hybrid polymer-NASICON nanocomposites.
- ii) Understanding of electrical transport mechanism and conductivity-structure correlation in novel hybrids.
- iii) To enhance the electrical transport and improve cation ( $\text{Na}^+/\text{Li}^+$ ) transport number in these novel composites.
- iv) To explore the possible use of these hybrids as electrolytes, particularly in  $\text{Na}^+$  ion-based all-solid-state supercapacitors (ASSCs).

To achieve the above objectives, the following systems have been chosen for investigation, and XAS along with XPS characterization have been explored to comprehend the conductivity-structure correlation.

- (i)  $5\text{LiCF}_3\text{SO}_3\text{-}95[\text{PEO}_{1-x}(\text{LiTi}_2(\text{PO}_4)_3)_x]$  where,  $0 \leq x \leq 0.9$ .
- (ii)  $5\text{LiCF}_3\text{SO}_3\text{-}95[\text{PEO}_{1-x}(\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3)_x]$  where,  $0 \leq x \leq 0.7$ .
- (iii)  $10\text{NaI-}90[\text{PEO}_{1-x}\text{NTP}_x]$  where,  $0 \leq x \leq 0.7$ .
- (iv)  $10\text{NaCF}_3\text{SO}_3\text{-}90[\text{NTP}_x\text{PEO}_{1-x}]$  where  $x = 0, 0.4$  and  $0.7$
- (v)  $63\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}\text{-}37(\text{PEO}_{1-x}\text{NaI}_x)$  for  $x = 0.03 - 0.13$

Further, for both the  $\text{Na}^+$  and  $\text{Li}^+$  ion-based systems, supercapacitors have been fabricated and characterized. Interesting findings have been reported.

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