

Polymer electrolytes for lithium ion batteries: a critical study

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Abstract Polymer electrolytes (PEs) are an essential component being used in most energy storage/conversion devices. The present review article on a brief history, advantage, and their brief application of polymer electrolyte systems. It consists of a glimpse on liquid, gel, and solid polymer electrolyte and a contrast comparison concerning benefits/disadvantages among the three. The article started with a brief introduction of polymer electrolytes followed by their varieties and extreme uses. The role of host polymer matrix by taking numerous examples of polymer electrolyte published by the different renowned group of the concerned field has been explored. The criteria for selection of appropriate host polymer, salt, inorganic filler/clay, and aprotic solvents to be used in polymer electrolyte have been discussed in detail. The mostly used polymer, salt, solvents, and inorganic filler/clay list has been prepared in order to keep the data bank at one place for new researchers. This article comprises different methodologies for the preparation of polymer electrolyte films. The different self-proposed mechanisms (like VTF, WLF, free volume theory, dispersed/intercalated mechanisms, etc.) have been discussed in order to explain the lithium ion conduction in polymer electrolyte systems. A numerous characterization techniques and their resulting analysis have been summarized from the different published reports at one place for better awareness of the scientific community/reader of the area.

Keywords Polymer electrolytes · Lithium ion battery · TEM · FTIR · Electrochemical analysis · Transport mechanism

Abbreviation

AFM	Atomic force microscope
AgNO ₃	Silver nitrate
Al ₂ O ₃	Aluminium oxide
AlCl ₄	Tetrachloroaluminate
ALE	Aqueous liquid electrolyte
BaTiO ₃	Barium titanate
ACN	Acetonitrile
CNT	Carbon nanotube
CPE	Composite polymer electrolyte
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DN	Donor number
DSC	Differential scanning calorimetry
EC	Ethylene carbonate
EDX	Energy-dispersive X-ray spectroscopy
ESW	Electrochemical stability window
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
GPEs	Gel polymer electrolytes
IL	Ionic liquid
LIB	Lithium ion battery
LiBETI	Lithium- <i>bis</i> perfluoroethylsulfonyle imide
LiBF ₄	Lithium tetrafluoroborate
LiBOB	Lithium <i>bis</i> (oxalato)borate

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LiCF ₃ SO ₃	Lithium trifluoromethanesulfonate
LiClO ₄	Lithium perchlorate
LiCoO ₂	Lithium cobalt oxide
LiDFOB	Lithium difluoro(oxalate)borate
LiFePO ₄	Lithium iron phosphate
LiPF ₆	Lithium hexafluorophosphate
LiTFSI	Lithium <i>bis</i> -trifluoromethanesulfonimide
LLTO	Lithium lanthanum titanate
LPEs	Liquid polymer electrolytes
Mg(NO ₃) ₂	Magnesium nitrate
MMT	Montmorillonite
NaClO ₄	Sodium perchlorate
NALE	Non-aqueous liquid electrolyte
NaPF ₆	Sodium hexafluorophosphate
NaPO ₃	Sodium hexametaphosphate
NM	Nitromethane
NMP	<i>N</i> -methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
P(AN- <i>co</i> -MMA)	Poly(acrylonitrile- <i>co</i> -methyl methacrylate)
PAN	Poly(acrylonitrile)
PC	Propylene carbonate
PCL	Poly(ϵ -caprolactone)
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PEGDMA	Poly(ethylene glycol dimethacrylate)
PEMA	Poly(ethyl methacrylate)
PEO	Poly(ethylene) oxide
PEs	Polymer electrolytes
PMMA	Poly(methyl methacrylate)
PNC	Polymer nanocomposite
PPO	Poly(propylene oxide)
PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVB	Polyvinyl butyral
PVC	Poly(vinyl chloride)
PVdF	Poly(vinylidenedifluoride)
PVdF-HFP	Poly(vinylidenedifluoridehexafluoropropylene)
SAED	Surface area electron diffraction pattern
SiO ₂	Silicon oxide
SnO ₂	Tin dioxide
SPEs	Solid polymer electrolytes
Sr ₂ O ₃	Strontium oxide
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TiO ₂	Titanium oxide
VTF	Vogel–Tamman–Fulcher
WLF	Williams–Landel–Ferry

XRD	X-ray diffraction
ZrO ₂	Zirconium oxide

Introduction

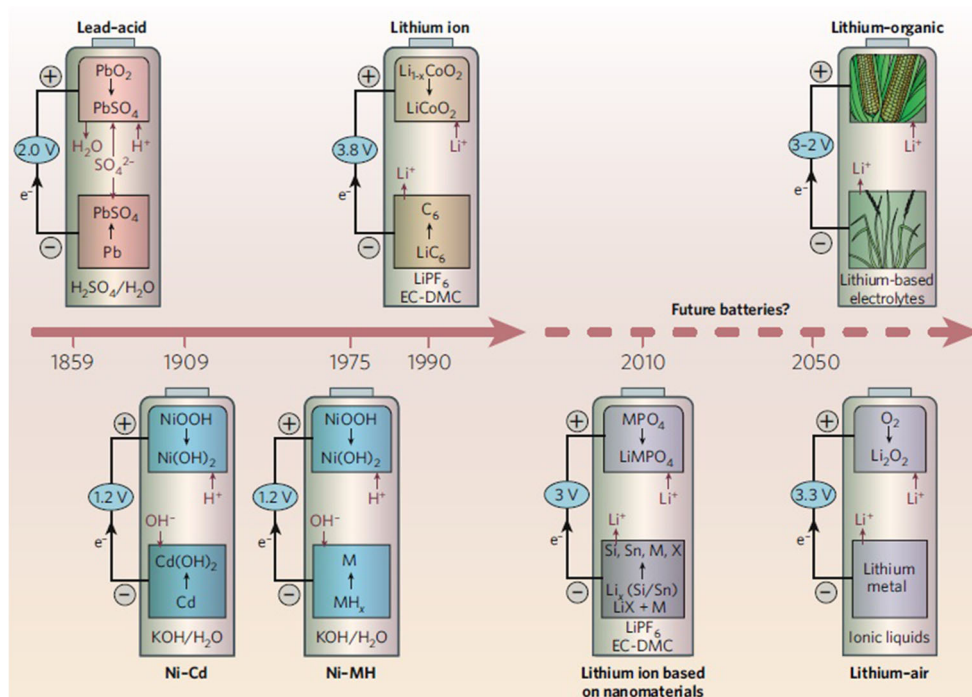
The worldwide development of secondary lithium ion batteries (LIBs) has received an extraordinary significance in the last three decades due to increasing demand for safe, reliable, and high energy-density storage/conversion devices such as lithium ion batteries, supercapacitor, fuel cell, etc. [1, 2]. The first report by Armand in 1970 suggested the use of polymer electrolytes (PEs) for LIBs with improved energy density and efficiency. With this trust, many prominent researchers all over the globe have focused towards the preparation of polymer electrolytes as a separator cum electrolyte for the LIB application. Polymer electrolytes exhibit unusual properties like size flexibility, transparency, light weight, ease of formation, elasticity, and ability to form good electrode/electrolyte contact. A battery consists of many electrochemical cells arranged in series or parallel manner. A single cell contains two electrodes and an electrolyte consisting of salts which provide the path for ion migration from the cathode to anode and vice versa.

1. Cathode (positive electrode)
2. Anode (negative electrode)
3. Electrolyte cum separator

Beside electrodes, the separator cum electrolyte is an essential component of the battery, as it plays a significant role in the transportation of ions during charging and discharging processes, so it must be in stable form during battery operation. Electrolytes have two active tasks; one is to conduct ions efficiently and second is to separate the electrodes to avoid short circuiting.

First-time lithium ion battery came into the market in 1991, by SONY Company. In this, LiCoO₂ was used as a cathode, graphite as anode, and insertion/extraction of ions takes place between both of them. Among the electrolytes, Li⁺ salt solution is preferred due to being light in weight, safety in handling, less steric hindrance, and wider potential window which facilitate the high energy density. It also exhibits the highest oxidation potential of any element, properties that make lithium ideally suitable for high energy-density batteries [3, 4]. The energy stored in LIBs was 180 Wh kg⁻¹ with an average voltage of 3.8 V and is five times greater than lead–acid batteries. It may seem inferior in the light of Moore’s law in electronics (according to which memory capacity doubles every 2 years), but it still took a revolution in material science to achieve it. Figure 1 shows the progress in battery technology with years and future development [5, 6]. There are various existing cell systems such as lead–acid, Ni–Cd, Ni–MH, Li–

Fig. 1 Battery chemistry over the years. Present-day battery technologies are being outpaced by the ever increasing power demands from new applications. As well as being inherently safe, batteries of the future will have to integrate the concept of environmental sustainability (reprinted by permission from [5], copyright Nature 2008)



ion, and Li metal which fulfills about 60% consumption of energy demand for electric devices. But among these, Li-ion batteries is superior to all existing systems due to its safety, high energy density, light weight, shape flexibility, and cost efficient.

Figure 2 shows gravimetric power and energy densities for different rechargeable batteries. The field of polymer electrolytes is an emerging class of solid-state ionic conductors (SSICs), and its presence in the research community, especially on polymers, is achieving new heights

with the passage of time. Mostly fast ionic conductors are based on inorganic materials with excellent transport properties, but poor electrolyte stability limits their use as electrolyte cum electrode separator. As during charging and discharging of a cell, there are volume changes observed, so a flexible and soft material needs to be used as the separator. The ionic conduction in polymer electrolytes occur only at above glass transition temperature (T_g), and their low conductivity value is compensated by the shape, size, and flexibility of electrolyte.

Fig. 2 Gravimetric power and energy densities for different rechargeable batteries. Most of these systems are currently being investigated for grid storage applications (reprinted with permission from [7], copyright Science 2011)

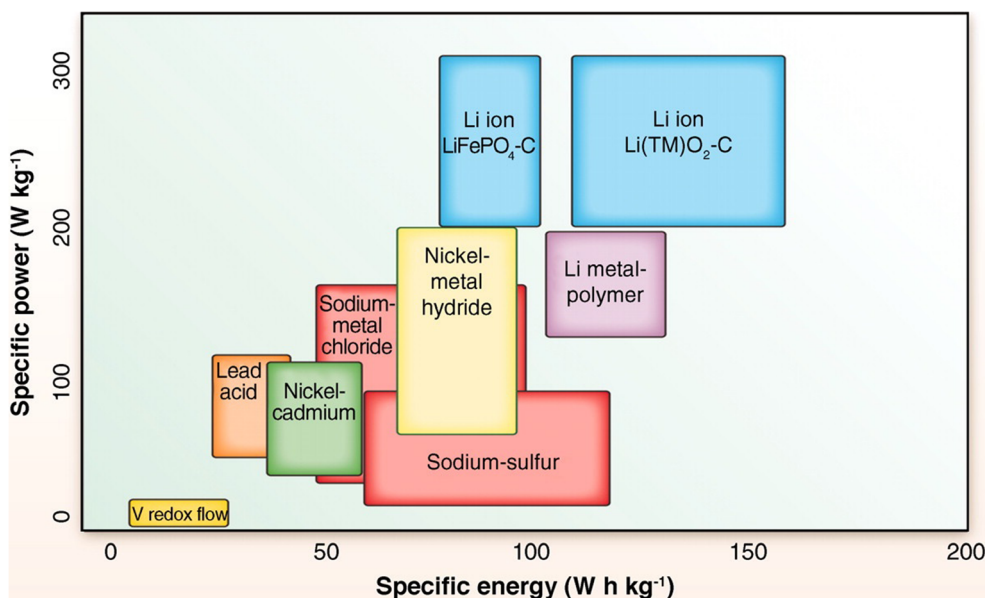


Fig. 3 Complex formation between poly(ethylene oxide) (PEO) and various metalsalts.+,Complex formed;-no evidence of complex (reprinted with permission from [14], World Scientific)

H															
⁺ Li ⁺	Be														
⁺ Na ⁺	⁺ Mg ⁺														
⁻ K ⁺	⁺ Ca ⁺	⁺ Sc ⁺	⁺ Ti ₃	⁺ V ₂	⁺ Cr ₂	⁺ Mn ⁺	⁺ Fe ⁺	⁺ Co ₂	⁺ Ni ⁺	⁺ Cu ₂	⁺ Zn ⁺	Al			
⁻ Rb ⁺	⁺ Sr ⁺	⁺ Y ⁺	⁺ Zr ₄	⁺ Nb ₅	⁺ Mo ₆	Tc	Ru	Rh	⁺ Pd ⁺	⁻ Ag ⁺	⁺ Cd ⁺	In	⁺ Sn ₂	⁺ Sb	
⁻ Cs ⁺	⁻ Ba ⁺	⁺ La ⁺	Hr	⁺ Tb ⁺	⁺ W ₆	Re	Os	Ir	Pt	Au	⁺ Hg ₂	⁺ Ti ₁	Pb	⁺ Bi ₃	Po
Fr	Ra	Ac													
⁺ Ce ⁺	⁺ Pr ⁺	⁺ Nd ⁺	Pm	⁺ Sm ⁺	⁺ Eu ⁺	⁺ Gd ⁺	⁺ Tb ⁺	⁺ Dy ⁺	⁺ Ho ⁺	⁺ Er ⁺	⁺ Tm ⁺	⁺ Yb ⁺	⁺ Lu ⁺		
Th	Pa	⁺ UO ₂													

Br⁻ — [] — I⁻

Cl⁻ — [] — [ClO₄]⁻, [CF₃SO₃]⁻

The phenomena of ionic conduction was identified by Michael Faraday in the 1800s on solid electrolytes PbF_2 ; later in 1964, first-time polymer electrolytes came in existence which was based on multivalent salts HgCl_2 and CdCl_2 . As multivalent cations are easier to handle and inexpensive than commonly used alkali metal salts, the presence of both crystalline phase and amorphous phase makes trying to study the properties of polymer electrolytes correctly [7, 8]. The first report of ionic conductivity in polymers was given by Peter V. Wright and Fenton-based on poly(ethylene oxide) (PEO) with alkali iodide salts. Later in 1978, Armand utilized PEO/alkaline salt compound in batteries as an ionic conductor. It was studied that this type of complex is capable of transporting ions in solid phase with mechanical flexibility, good interface contact, and used as electrolytes in electrochemical devices [9–11]. A wide variety of electrolytes using salt and polymer host were prepared based on lattice/dissociation energy of dopant salt. In any battery system, the electrolyte along with a separator serves as a medium for transportation of ions and to keep electrodes separately when liquid electrolytes are used. For the solid-state lithium ion batteries, the polymer electrolyte is used as a thin-film membrane which can function for both ion conduction and separation of electrodes. The selection criteria for preparation of PEs depend on the delocalized charge of anion which directly depends on the lattice energy of the corresponding salt [12]. Polymer electrolytes formed by dissolving Li salt in a high molecular weight polymer host such as PEO are dual ionic conductors. But the collective movement of both cation and anion may lead to concentration polarization resulting into damage of battery [13]. So, the above problem can be eliminated by using single ion conductor either cation or anion as the charge carrier. Most of the work is focused towards Li cation of salt of electrolyte due to smaller cation size. Almost all the salt of the periodic table is doped in polymer host to form solid polymer electrolyte as shown in Fig. 3. The polymer chain itself acts as solvent for salt which become dissociated and results in electrolyte behavior.

The fundamental difference between electronically and ionically conducting polymers is that the latter (colorless) donate electron pairs from heteroatoms included in the macromolecular array from “s” orbitals to Lewis acids (cations), while the former (highly absorbing) release single electrons from their conjugated “ π ” system upon oxidative doping, with the formation of polarons (radical cations) possibly as dimers (bipolarons). Polymer electrolytes are to solutions what redox polymers (polypyrrole and polythiophene) are to metals. As a rule, electronic conductivity is best in conventional systems (crystalline region) while ionic conductivity prefers disordered matter (amorphous region) [15]. Polymers can exist in amorphous or semi-crystalline phase, depending on the regularity and length of the chain. Initially, crystalline regions were supposed to be ion transportation area with the ions moving along the PEO helices as the primary mechanism. But later, it was soon confirmed that the amorphous phase alone gives rise to ion transport [4, 16]. The segmental motion of the disordered chains takes place above the T_g (a consequence of the third law of thermodynamics), in the amorphous region only. Polymers with low T_g are preferred for fast ion transport and excellent flexibility in the electrolyte. Therefore, ionic transport is strictly correlated with the segmental motion of polymer chain, flexibility and degree of amorphousness.

Polymer electrolytes

Polymer electrolytes (PEs) are a class of materials introduced in the 1970s, which became the promising candidate for ion conducting material in energy storage/conversion devices with high ionic conductivity, improved stability properties, and safety as compared with organic liquid electrolytes.

PEs consist of a macromolecule matrix with low lattice energy salt dissolved in a low viscosity and high dielectric constant organic solvents with properties such as good ionic conductivity, high chemical stability, low cost, and safety. The principle of ionic conduction in the polymer electrolytes is the

formation of covalent bond between the polymer backbones with the ionizing groups. Initially, the electron donor panel in the polymer forms salivation to the cation component in the dopant salt and then facilitates ion separation, leading to ionic hopping mechanism which generates the ionic conductivity. For proper complex formation of polymer and salt, the lattice energy of the salt should be small and the dielectric constant (ϵ) of the host polymer should be high. The ionic conduction of polymer electrolytes takes place from the rapid segmental motion of polymer matrix combined with strong Lewis-type acid–base interaction between the cation and donor atom. Unfortunately, the use of a Li metal anode in combination with liquid electrolytes often leads to safety problems associated with the formation of irregular metal deposits during recharging which can result in Li dendrite formation. Such dendrites can form internal short circuiting due to the thread-like structure between the electrodes and may cause rapid discharge leading to uncontrolled thermal runaway. The use of lithium ion-conducting polymer electrolytes could eliminate some of the safety problems encountered when using liquid electrolytes due to reduced flammability and higher resistance to dendrite formation but is hindered by conductivities which are typically much lower than those of liquid electrolytes at room temperature [17].

Polymer electrolytes have many advantages like high ionic conductivity, high energy density, solvent-free condition, structural stability, low volatility, wide electrochemical stability window, ease of formation, and being light in weight. Polymer electrolytes are solutions of salts dissociated in the polymer host with electron donor group. As polymer electrolytes play dual role both as a separator and an electrolyte in a solid-state configuration, it must possess many essential electrochemical characteristics as listed below [18]:

1. High ionic conductivity ($>10^{-4}$ S cm $^{-1}$) at room temperature
2. Minimum electronic conductivity ($<10^{-6}$ S cm $^{-1}$)
3. Non-volatility
4. High cationic transference number (t_{ion})
5. Excellent chemical, thermal, and mechanical stabilities
6. Good compatibility with the electrode materials
7. Low activation energy for ionic conduction
8. Broad operating range of temperature
9. Environment friendly
10. Inexpensive and improved safety
11. Low toxicity, low weight, and easy availability
12. Low glass-transition temperature T_g

Polymer electrolyte overcomes many drawbacks faced in liquid electrolytes in terms of shape flexibility, size, and weight. The fast ion transport occurs in amorphous phase with two or three orders of magnitude higher conductivity when compared with crystalline phase. Table 1 summarizes the

properties, advantages, and application of polymer electrolytes.

Solid polymer electrolytes (SPEs) have captured much weightage from the last few years because of their abrupt application in rechargeable lithium ion polymer batteries, fuel cells, electrochromic display devices, and electric vehicle, aerospace, automobile, and electronic industries [1, 19]. Although, preparation of polymeric electrolytes using various host polymers such as poly(acrylonitrile), poly(propylene oxide), poly(methyl methacrylate), and poly(maleic anhydride-styrene) have been studied. Among all the high molecular weight PEO-based polymer electrolytes are best candidates for polymer matrix due to their great salivation power and ion transport mechanism [20–24]. From exhaustive literature survey, the PEs are broadly divided into three categories. The description of all three types is discussed below.

Liquid polymer electrolytes (LPEs)

Liquid electrolytes consist of a lithium salt dissolved in an organic solvent and a separator which prevent the short circuiting of electrodes. Lithium ions migrate within the cell between positive and negative electrodes during charge and discharge cycles of the battery. Mostly used lithium salts are LiClO $_4$, LiPF $_6$, and LiBF $_4$. Depending on the solvent used, it can be divided further into non-aqueous liquid (NALE) and aqueous liquid electrolyte (ALE). NALE have high ionic conductivity than solid polymer electrolyte and are obtained by dissolving alkali salts in solvents (ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), etc.). They possess attractive properties such as high ionic conductivity, thermal stability at the ambient/subambient conditions, relatively large electrochemical stability window, and ease of handling [25–31]. ALE has more ionic conductivity than NALE and properties such as non-flammable nature and inexpensive along with safety, making it the suitable candidate for practical use even at the higher temperature. Ionic liquids (ILs) are a new class of purely organic salts like materials and exist in liquid form at room temperature due to weak ion coordination/poor packing of atoms. IL have lower melting point below room temperature and are usable over a wide temperature range (300–400 °C) from the melting point to the decomposition temperature of the ionic liquid. The solvation properties of these ionic liquids and wide electrochemical stability make them the suitable candidate to replace organic electrolyte for the development of advanced electrochemical devices like batteries, fuel cell, supercapacitors, etc. [32–34]. Ionic liquids are highly tunable with both changing the ratio of cation to anion and using a different cation or anion can drastically change solvent properties. Table 2 shows some of liquid polymer electrolytes (LPEs) and their conductivity values.

Table 1 Properties, advantages, and applications of polymer electrolytes

Polymer electrolytes		
Properties	Advantages	Applications
Transparent	Ease of fabrication	Electrochromic window
Solvent free	Long life span	Solid-state batteries
Lone pair electrons	To attract cations for coordination bond	Solid-state batteries
Light weight	Restricts use of corrosive solvent	Solar cells, fuel cells
Chemical and thermal stability	High flashing point	Solid-state batteries
Flexible geometry	No production of harmful gases	Supercapacitor
Thin-film forming ability	Prevent leakage	Mobile cellular phone
Wide electrochemical windows	Dendrite growth suppression	Electrochemical sensors
Improved safety	Reduced flammability	Analog memory devices
Versatility	Low cost	Electric vehicles
High ionic conductivity	Non-toxic	Electrochromic display devices
Low self-discharge	No internal shorting	Solid-state batteries
Compatibility with electrodes	Provide the easy path for ion migrations	Solid-state batteries
Reliability	Reproducibility of the parameters	Solid-state batteries

Gel polymer electrolytes (GPEs)

Gel polymer electrolytes (GPEs) are third-generation PEs which consist of an inert polymer matrix in which a solvating, low molecular weight compound, and a lithium salt are dissolved. Gels can be classified into two categories from method of sample preparation [8, 49]:

1. Physical gels—liquid electrolyte is confined in a polymer matrix without may bond formation between polymer and solvent, e.g., LiClO₄/EC/PC in poly(methyl methacrylate) (PMMA).
2. Chemical gels—a crosslinker leads to the formation of chemical bond between the functional group of polymer and crosslinker agent.

The lithium salt is responsible for conduction in polymer matrix, and polymer holds the electrolyte to provide mechanical strength. The GPEs show better ionic conductivity, wide electrochemical stability window (ESW), and good compatibility with electrodes because of enhanced ionic mobility. GPEs carry both cohesive properties of solids and diffusive properties of liquids and a good mechanical strength [8]. In GPEs, the role of the polymer is to sustain a solid-state matrix which supports the ion migration in solvents and conductivity value of about 10^{-3} S cm⁻¹ at ambient temperature can be achieved. Here, electrolyte can play the role of plasticizer and lower the glass transition temperature which results in faster ionic conduction. Gel polymer electrolytes are also known as polymer hybrids. Plasticizers having little evaporation solvents such as EC, PC, DEC, and DMC are used as

Table 2 Some important liquid polymer electrolyte and their properties

Polymer	Salt/ILs	Solvent	Conductivity	Ref.
PEO-PVdF	LiTFSI	Acetone/DMAc	4.9×10^{-3}	[36]
PVdF-HFP	[BMIM][BF ₄]	Acetone	1.6×10^{-2}	[37]
PVA	LiClO ₄ /[EMIM][EtSO ₄]	DMSO	1.9×10^{-6}	[38]
PVdF-HFP	PAni-MMT/ BMIMBr	Acetone	7.7×10^{-3}	[39]
PEO	LiTFSI/BMITFSI	Solvent free	3.2×10^{-4}	[40]
PEMA	NH ₄ CF ₃ SO ₃ /BMATFSI	THF	10^{-4}	[41]
PEO	LiTf/EMITf	Acetonitrile (ACN)	3×10^{-4}	[42]
PVA	CH ₃ COONH ₄ /(BmImCl)	Distilled water	7.3×10^{-3} (at 120 °C)	[43]
PVA	Li ₂ SO ₄ /BMIMCl	—	37×10^{-3}	[44]
PEO	LiPF ₆ /MMPIPF ₆	—	1.13×10^{-3}	[45]
PEO	EMIM-TY	Solvent free	10^{-4}	[46]
PEO	LiClO ₄ /[BMIM][PF ₆]	Anhydrous methanol	8×10^{-6}	[47]
PEO	Al ₂ O ₃ /EMIM-TY	Distilled methanol	5.8×10^{-5}	[48]
PEO	LiTFSI/[Py ₁₄ TFSI] _{1.92}	—	1.1×10^{-4}	[49]

Table 3 Some important gel polymer electrolyte and their properties

Polymer	Salt	Solvent	Conductivity	ESW (V)	Ref.
PVdF-HFP	NaClO ₄ -EC/DMC/DEC	DMF	0.60×10^{-3}	4.6	[51]
P(EO-co-PO)	LiPF ₆	DMF + distilled water	2.8×10^{-3}	5.1	[52]
P(MMA-AN-VAc)	LiPF ₆	DMF	3.48×10^{-3}	5.6	[53]
PMMA	ZnTr	EC/PC	1.67×10^{-3}	5	[54]
PVdF	LiBF ₄ -EC/PC	No solvent	6×10^{-3}		[55]
PMMA	LiN(CF ₃ SO ₂) ₂	EC/DMC	1×10^{-3}		[56]
PVdF-HFP	LiN(CF ₃ SO ₂) ₂	EC/DEC	10^{-3}		[57]
PVS-PVdF	LiN(SO ₂ CF ₃) ₂	EC/PC	1.74×10^{-3}	3.9–4.3	[58]
PVdF	SiO ₂ -PAALi-EC/EMC/DMC	DMF/acetone	3.5×10^{-3}	5.05	[59]
P(HFBMA-co-PEGMA)/PVDF		—	3.19×10^{-3}	4.5	[60]
PVdF	LiPVAOB	—	0.26×10^{-3}		[61]
PAN-PMMA	PYR14TFSI	—	3.6×10^{-3}	5	[62]
PVDF-HFP	PLTB-EC/DMC	DMF	0.45×10^{-3}	5	[63]
PECA-PET	LiPF ₆	Acetone	2.54×10^{-3}	4.7	[64]
PVdF-PEO	LiClO ₄ -EC/PC/DVB	—	3.03×10^{-3}	5	[65]
PEMA	LiBF ₄ -EC/EMC/PC	THF	5.8×10^{-4}	4.3	[66]
PVdF-PEMA	LiClO ₄ -EC/PC	THF	1.47×10^{-4}	4.5	[67]
PVA	NH ₄ SCN	DMSO	2.58×10^{-3}		[68]
P(MA-co-AN)/PVA	LiPF ₆ -EC/DMC/DEC	—	0.98×10^{-3}	5.2	[69]
PVB	LiPF ₆	—	4.09×10^{-4}	1.6–5.0	[70]
PVdF-HFP	Urea/PVP	DMF	2.823×10^{-3}	5	[71]

plasticizers in many polymer salts (Table 3). GPEs facilitate us with advantages such as various shapes availability, increased rate of charging/discharging, light weight, cost-effective, and higher power density [5, 31]. They have better ionic conductivity but have lower mechanical stability [71].

Solid polymer electrolyte (SPEs)

SPEs are preferred over LPEs and GPEs due to many advantages, such as high durability, long shelf life, high energy density, light in weight, great flexibility for cell design, low reactivity towards the electrodes, eliminate the problems of solvent leakage and harmful gas for above ambient temperature operations, and reduce packaging cost. It also shows wider electrochemical and thermal stability range as well as low volatility [72]. Solid polymer electrolyte (SPEs) consists of dissolution of salt in a polymer matrix with electron donor group and have various advantages like design flexibility, miniaturization feasibility, improved safety, ease of device fabrication, etc. Furthermore, an ionically conducting polymer membrane for electrochemical device applications should have a proper balance between its electrical conductivity and mechanical strength (i.e., high ionic conductivity and excellent mechanical strength) under the conditions desirable for a particular application. SPEs having optimized conductivity and stability properties under ambient and subambient conditions may be expected to have

the potential for applications in solid-state ionic devices such as the high energy-density lithium ion batteries, supercapacitors, fuel cell, etc. [73]. When lithium salt is added in the polymer system, it gets dissociated by interaction with the polar group of polymer and lithium ions move along the long polymer chains by hopping process in amorphous phase provided by polymer [74].

Selection criteria and properties of polymer host/salt/nanofiller/solvent

Table 4 shows some mostly used polymer electrolyte with their properties.

Properties for polymer host

1. Must have electron donor groups such as $\ddot{O}$, N, and S for coordinating with ions.
2. Provide fast segmental motion of polymer chain
3. Low glass transition temperature
4. High degradation temperature
5. High molecular weight
6. Spatial conformation for more salt dissociation

Table 4 Some important solid polymer electrolyte and their properties

Polymer	Salt	Filler/plasticizer	Solvent	Conductivity (S/cm)	Thermal stability (°C)	ESW (V)	Ref.
PVA	Mg(NO ₃) ₂		Triply distilled water	7.36×10^{-7}			[76]
PAN	LiClO ₄	ALA-MMT	DMF	2.44×10^{-4}		4.75	[77]
PVC-PEMA	LiPF ₆		THF	10^{-3}		4.3	[78]
PEO	LiTf	EC/sepiolite	–	10^{-4}		4.5	[79]
PEO-PMMA	LiClO ₄	PA	NMP	1.59×10^{-5}	209	>5	[80]
PVA-PVdF	LiClO ₄		DMF	3.03×10^{-5}	273		[81]
PEO-PMMA	LiTFSI	Al ₂ O ₃	THF	3.24×10^{-4}		4.6	[82]
PVdF-PVA	LiTFSI	MMT	DMF	4.31×10^{-4}		4.7	[83]
PAN	LiPF ₆	DMMT	DMF	3.7×10^{-3}	200	4.3	[84]
PAN	LiCF ₃ SO ₃	DMMT	DMF	10^{-3}	250	5.6	[85]
PEO	LiClO ₄	SiO ₂		1.2×10^{-3}		5.5	[86]
PEO	LiAsF ₆	MMT	ACN	4×10^{-5}			[87]
PEO	LiCF ₃ SO ₃	Al ₂ O ₃ -DOP	–	7.60×10^{-4}			[88]
PAN-PVA	LiClO ₄	EC/DMC	EC/DMC	2.5×10^{-4}	300	4.8	[89]
PVA-PVdF	LiCF ₃ SO ₃		DMF	2.7×10^{-3}	175	3.4	[90]
PEO	LiFSI		ACN	1.3×10^{-3}		5.7	[91]
PVA	NH ₄ Al(SO ₄) ₂ · 12H ₂ O		Water	1.73×10^{-4}	~350		[92]
PVC-PEMA	LiClO ₄	PC	THF	3.45×10^{-3}	230		[93]
PVA	Cu(NO ₃) ₂		–	1.6×10^{-5}			[94]
PMMA	LiClO ₄	PC	–	7.04×10^{-3}	~240		[95]
PVB	LiClO ₄	PEG	–	2.15×10^{-6}			[96]
PVdF-PAN	NaHCO ₃	SiO ₂	–	3.32×10^{-3}		5	[97]

A brief summary of most frequently used host polymers have been discussed below.

Poly(ethylene oxide) (PEO)

Since in 1973 Wright discovered ionic conductivity in PEO-Li⁺ salt complexes, significant research efforts have been devoted on PEO as host polymer due to ease of fabrication and conduction occurring between ether group of PEO and Li ions. But low conductivity value of PEO (10^{-8} S cm⁻¹) due to crystalline nature at ambient temperature restricts its use in advanced energy storage devices. However, ionic conductivity may be improved further by the addition of plasticizer in PS complex, but the presence of hydroxyl end groups reduces the interfacial properties at electrode/electrolyte interface [97, 98, 100]. Kelly et al. [98] studied the role of various additives in the enhancement of conductivity in PEO-Li⁺ systems, and it was concluded that melting and glass transition temperature of the polymer decreases on the partial substitution of high molecular weight of the polymer by a PEO of low molecular weight. Fauteaux et al. [99] demonstrated the electrochemical stability and ionic conductivity measurements for high molecular weight PEO-based solid polymer electrolytes for electrochemical devices. Ito et al. [100] examined the effect of PEG plasticizer bases on PEO-LiCF₃SO₃ complexes on ionic

conductivity. An increase in ionic conductivity was observed with increase in PEG content and attributed to the reduction of crystallinity with an increase in free volume of the system. But the presence of hydroxyl end groups in PEG restricts its use due to poor interfacial properties.

Poly(acrylonitrile) (PAN)

In later years, poly(acrylonitrile) (PAN) was examined as host polymer due to its two main key factors: (i) small thermal resistance and (ii) flame retardant behavior. It also provides a homogenous, hybrid electrolyte films on the dispersion of plasticizer and salt. The ionic conductivity of PAN-based gel electrolyte is between 10^{-5} and 10^{-3} S cm⁻¹, and the amount of transferred lithium ion is larger than PEO-based gel polymer electrolyte as reported by Feuliade et al. [101]. An increase in ionic conductivity of PAN-based electrolytes consisting of 38 mol% of EC, 33 mol% of PC with 8 mol% of LiClO₄, and 21 mol% of PAN was reported by Abraham and Alamgir [102]. The electrochemical properties of gel electrolytes by immobilization of PAN matrix with different lithium salts Li⁺-X⁻ (X = ClO₄⁻, AsF₆⁻, (CF₃SO₂)₂⁻) were reported by Croce et al. [103]. It showed ionic conductivity and high lithium ion transference number, but their application in rechargeable lithium polymer batteries is less due to the

instability of lithium electrode interface. An entirely amorphous gel-based PAN-LiClO₄ in EC showed room temperature conductivity of the order of 10^{-3} S cm⁻¹ at ambient temperature and transference number of more than 0.5 because of the absence of ether group in the PAN matrix as studied by Appetecchi et al. [104]. Two types of gel electrolytes by taking PAN as host, EC/DMC as plasticizers with LiPF₆ or LiCF₃SO₃ as salt were reported by Appetecchi et al. [105]. The result showed that membranes have high ionic conductivity, wide electrochemical stability window. Despite the several advantages of PAN-based electrolytes, like high ionic conductivity of the order of 10^{-3} S cm⁻¹ at 20 °C, an excellent electrochemical stability of 4.5 V and a lithium transference number around 0.6, its poor compatibility with lithium metal anode offsets from practical applications. It was reported that the lithium electrode undergoes severe passivation when in contact with PAN-based electrodes and affects cyclability and ultimately leads to safety hazards. The main issue noticed during PAN as host polymer was the developed internal resistance of the battery. The above problems can be eliminated by blending of PAN and PEO which improves the ionic conductivity, mechanical flexibility, and interfacial properties at electrode/electrolyte interface [106].

Poly (methyl methacrylate) (PMMA)

PMMA-based PEs are also under investigation due to their lower cost and enhanced interface stability than other polymer hosts. But the poor mechanical flexibility of the film restricts its use as electrolytes in energy storage devices. However, some studies reported that copolymerization of PMMA with another polymer improves the mechanical and electrical properties of the polymer electrolyte. Poly(vinyl chloride) (PVC) copolymerized with PMMA increases the conductivity of GPEs as reviewed by Ramesh et al. [107]. Porous poly(ethylene glycol dimethacrylate)–carbon nanotube (PDMS-CNT) nanocomposites with PMMA improved the flexibility, and controlled phase separation between PDMS and PMMA is observed by Lee et al. [108].

Poly(vinylidenedifluoride) (PVdF)

Recently, studies show that poly(vinylidenedifluoride) (PVdF) having semi-crystalline structure is also emerging as a host polymer for the electrolyte in battery system due to its high dielectric constant ($\epsilon = 8.4$) and the presence of strong electron-withdrawing functional groups (–C–F) which helps for greater dissolution of lithium salts and subsequently supports the high concentration of charge carriers. As high dielectric constant helps for more significant dissolution of lithium salts and consequently supports the high concentration of charge carriers, functional group induces a net dipole moment [109]. Although the mobility of PVdF-based GPEs is greater

than other polymer host matrix materials, the ionic conductivity of GPEs is still lower than liquid electrolytes. Introducing ionic liquids or nanosized fillers in GPE system could help to improve the performance of lithium ion polymer batteries. The plasticized Tsuchida et al. [110, 111] examined PVdF with 30 mol% of LiClO₄ complex, and it was found that the viscosity dominates over dielectric constant of the plasticizer during conductivity study and is of the order of 10^{-5} S cm⁻¹ due to membrane homogeneity. Choe et al. [57] examined a plasticized PVdF-based electrolytes with a solution of LiN(CF₃SO₂)₂ in PC which offers conductivity of 1.74×10^{-3} S cm⁻¹ at 30 °C and oxidation potential limits between 3.9 and 4.3 V vs. Li⁺/Li. It was concluded that incorporation of plasticizer enhances conductivity value by two to four orders. Also, the cyclic voltammetry studies suggested that PVdF electrolytes are more suitable for primary than secondary batteries when lithium metal is employed as the anode and may have good shelf life [112]. Although the PVdF-based electrolytes have good electrochemical properties, presence of fluorinated polymer makes it unstable towards lithium leading to reduced interfacial properties between lithium and fluorine.

Polyvinyl pyrrolidone (PVP)

Polyvinyl pyrrolidone (PVP) is used as polymer host due to its properties such as its amorphous nature and presence of carbonyl group (C=O) in the side chains of PVP. It quickly gets dissolved in many polar solvents. It can provide excellent thermal and mechanical properties due to its crosslinking nature. Furthermore, PVP is highly soluble in polar solvents such as alcohol. Table 5 shows some commonly used polymer hosts with their glass transition and melting temperature.

Properties of salt as conducting species

Salt is one of two major components of any electrolyte. Among the properties directly affecting the salt is the solubility in the solvent for formation of more free charge carriers, wide potential stability window, non-toxic nature, and chemical and thermal stability. Spices used as conducting species in PE must have the following properties [18, 113]:

1. High thermal and chemical stability.
2. High ionic conductivity.
3. Low cost and easy processing.
4. The anion should be stable against oxidative decomposition at the cathode.
5. Form less-resistive solid-electrolyte interfaces on electrodes for cell safety and long-term cyclability.
6. Completely dissolve and dissociate in the non-aqueous media with high mobility.

Table 5 Properties of mostly used polymer host in polymer electrolytes

Abbreviation	Polymer name	T_g	T_m	Formula
PEO	Poly(ethylene) oxide	−67	65	$(-\text{CH}_2\text{CH}_2\text{O}-)_n$
PMMA	Poly(methyl methacrylate)	105	160	$(\text{C}_5\text{O}_2\text{H}_8)_n$
PVC	Poly(vinyl chloride)	81	160	$(\text{C}_2\text{H}_3\text{Cl})_n$
PVA	Poly(vinyl alcohol)	85	230	$(\text{C}_2\text{H}_4\text{O})_n$
PAN	Poly(acrylonitrile)	125	317	$(\text{C}_3\text{H}_3\text{N})_n$
PEMA	Poly(ethyl methacrylate)	66	160	$(\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{C}_2\text{H}_5))_n$
PS	Polystyrene	100	240	$(\text{C}_8\text{H}_8)_n$
PPO	Poly(propylene oxide)	−60		$-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_n$
PVdF-HFP	Poly(vinylidene fluoridehexafluoropropylene)	−65	135	$-(\text{CH}_2\text{CF}_2)_n(\text{CF}_2\text{CF}(\text{CF}_3))_m-$
PDMS	Poly(dimethylsiloxane)	−127	−40	$-(\text{SiO}(\text{CH}_3)_2)_n$
PVdF	Poly(vinylidene fluoride)	−40	171	$-(\text{CH}_2\text{CF}_2)_n-$
PC	Polycarbonate	147	230	–

- Both anion and cation should remain inert towards the other cell components, such as the separator/electrolyte and electrode substrates.
- The anion should be non-toxic, water stable and thermally stable

The ionic conductivity in a PEs is always dependent on the concentration of polymer and salt which is calculated using stoichiometry calculation. So, it becomes necessary to see the type of salt which is good that does not form ion pair or ion aggregation and also easily get dissociated in the solvent with the polymer. So, the salt with large anion radii are preferred for faster dissociation of salt due to electric charge delocalization and low basicity, and screened negative charge fulfills our requirement of cationic transference number (t_{cation}) equal to unity [114]. Ion mobility also depends on conductivity and varies with the glass transition temperature of the polymer. Also, at high concentration of salt unavailability of suitable coordinating sites in polymer host hinders the ion motion and effects the polymer segmental motion. Also, the ion transport depends on the dissociation rate, as it migrates via interacting with the polymer coordinating sites. At low concentration of salt, conductivity is almost independent on salt content, but with an increase in this more free charge carriers participate after dissociation in conduction process. Gray et al. [115] proposed a concept for solvation of cations in polymer electrolytes and suggested that formation of coordination bond due to partial sharing of the lone pair of electrons and energy change in PEs is dominated by cation solvation while solvation with anion is less due to weak interaction of the polymer with the anion. LiClO_4 was the most common lithium salts used in the lithium primary batteries. However, the high oxidability of anions (ClO_4^-) caused some safety issue in secondary batteries; thus, LiPF_6 replaced LiClO_4 in the newer designs and became the major material for electrolytes, which exhibits better overall performance including higher ionic

conductivity, more solubility, and broad chemical stability. One drawback of LiPF_6 as compared with other lithium salts is poor thermal stability and natural occurrence of hydrolysis. Basically, LiPF_6 decompose at 80 °C and produce high Lewis acidity PF_5 , gas and its reaction with solvent provide an internal pressure inside battery system which may lead to explosion [116]. Also, LiPF_6 is very sensitive to moisture and react with water [117]. Lithium *bis*-trifluoromethanesulfonimide (LiTFSI) has an excellent thermal stability with a decomposition temperature of 360 °C. The high dispersion of anionic charge of lithium salt makes it more easily ionized. Li-based salts are mostly used due to smaller cationic radii than Na ion and have more conductivity value due to faster transport between cathode and anode. Variation of some properties of lithium salts is shown in Table 6 [113]. Some fundamental properties and structure of lithium salts are given in Table 7.

Inorganic fillers/clay

Polymer electrolytes can be prepared by addition or incorporation of nanofiller and intercalation of clay in the polymer matrix. The addition of nanofiller/clay does not only enhance the conductivity but also improve the mechanical properties such as physical strength of PEs.

Inorganic filler

The particle size of the filler is a very important factor that affects the ion conduction. Ferroelectric fillers such as BaTiO_3 reduce the interfacial resistance between electrode/electrolyte surfaces due to the permanent dipole of ferroelectric materials [118]. The filler acts as a solid plasticizer that enhances the transport properties and reduces the crystallinity due to increase in the dielectric constant. Fillers must have low pressure in the temperature range of operation. Fillers with Lewis acid surface group interacts with both polymer and ion and

Table 6 Variation of some characteristics of lithium salts [113]

Stability of anion	$\text{CF}_3\text{SO}_3 < \text{ClO}_4 < (\text{CF}_3\text{SO}_2)_2\text{N} < (\text{CF}_3\text{SO}_2)_3\text{C} < \text{C}_4\text{F}_9\text{SO}_3 < \text{BF}_4 < \text{PF}_6 < \text{AsF}_6$
Oxidation potential	$(\text{CF}_3\text{SO}_3)^- (5.9 \text{ V}) < \text{ClO}_4^- (6.0 \text{ V}) < (\text{N}(\text{CF}_3\text{SO}_2)_2)^- = (\text{CF}_3\text{SO}_2)_3\text{C}^- (6.1 \text{ V}) < \text{BF}_4^- (6.2 \text{ V}) < \text{PF}_6^- (6.3 \text{ V}) < \text{AsF}_6^- < (6.5 \text{ V})$
Dissociation constant	$\text{LiTf} < \text{LiBF}_4 < \text{LiClO}_4 < \text{LiPF}_6 < \text{LiAsF}_6 < \text{LiTFSI} < \text{LiBOB}$
Average ion mobility	$\text{LiBF}_4 > \text{LiClO}_4 > \text{LiPF}_6 > \text{LiAsF}_6 > \text{LiTf} > \text{LiTFSI}$

reduces the ion coupling [119]. The polymer provides the path for conduction of ions, and filler affects the polymer stiffness to support the ionic transport. A high dielectric constant filler may also interact directly with the polymer host. There are various fillers which are presently used: BaTiO_3 [120], Al_2O_3 [121], TiO_2 [122], SiO_2 [123], and CeO_2 [124] result in an increase in ionic conductivity and mechanical properties of polymer membranes due to better thermal and structural compatibility of nanosized fillers than polymers. The plasticizer such as EC/PC helps in dissociation of salt and enhances the conductivity, but their use is limited due to its volatile and flammable nature. There are various classes of filler which affect the various properties of polymer electrolyte as shown in Table 8 [125].

Inorganic clay

Among the large numbers of layered solids, clay minerals especially the smectite group are most widely used for the reinforcement of polymer matrices and thus for the fabrication of polymer nanocomposites because of their unique structure and reactivity together with their high strength and stiffness and high aspect ratio of each platelet. Clay special features are as given below:

1. High aspect ratio
2. High cation exchange capacity (CEC)
3. Large specific surface area
4. Appropriate interlayer charge
5. Length scale

Solvents for polymer electrolyte

Polymer electrolyte serves as a medium for ion transport and prepared by dissolving the salt in a solvent (organic or inorganic water). Both conductive species and solvent interact with ion–dipole interaction [126]. The fundamental principle of solvation is the dissolution of one substance in a solvent, and during this process, solvent molecules get arranged via ion–dipole interaction at the molecular level around solute molecules. In the case of salt, the solute role is played by an ionic species and of the polar solvent by dipoles. The interaction force tells the energy of solvation required in the case of ionic solutes and is inversely proportional to the squared distance

between solute and solvent molecule. So, smaller ion results in more interaction force with greater dissolution in the solvent. Also, the solvation by the electrostatic interaction is in direct proportional with dipole moment (μ) of solvent. So, polar solvents such as water, nitrile, amide, etc. are used for better solvation due to high dielectric constant as suggested in a model by Born. The main properties of a solvent [19, 127] which are required for more dissolution of ions and high mobility are:

1. It should have a high dielectric constant ($\epsilon > 15$)
2. It should have low viscosity (≤ 1 cP)
3. It must have low melting point (T_m)
4. It must have high boiling point (T_b)
5. It should have low vapor pressure
6. It must be non-toxic and economic
7. Zero reactivity with electrode materials
8. Remain inert to the charged surfaces of the electrodes
9. High donor number (DN) for more dissociation of ion
10. Be safe, non-toxic and economical

Cyclic carbonates such as EC and PC are characterized by high dielectric constant values which dissociate more lithium salts and low volatility, but high viscosity value eliminates their transport properties [128]. Table 9 shows a list of commonly used solvents and their properties. Acetonitrile is also a good solvent due to moderate dielectric constant and low viscosity. Dimethyl formamide (DMF) is a mostly used solvent and is suitable for almost all polymers in electrochemical devices, but its high boiling temperature sometimes restricts its use. Two solvents can be mixed, one having high dielectric constant and the other having low viscosity for faster ion conduction.

The key requirement for a solvent is high dielectric constant and high flashing point (FP), former helps in dissociation of more salt and later improves the safety of energy storage device. Linear carbonates DEC and DMC have low dielectric constant and low viscosity. Cyclic carbonates EC and PC fulfill these requirements of high dielectric constant ($(\epsilon(\text{EC at } 40^\circ\text{C}) = 89.78 \text{ and } \epsilon(\text{PC at } 25^\circ\text{C}) = 64.92)$), high viscosity, and high flash point (FP (EC) = 150°C and FP (EC) = 132°C) [129]. High viscosity is due to the large mutual interaction between solvent particles. A combination of both EC and PC together could dissolve more lithium salt as compared with single solvent as reported by Li et al. [130]. Another approach

Table 7 Structure and properties of commonly used lithium salts for studies on polymer electrolytes (reprinted with permission from [115], copyright Elsevier 2014)

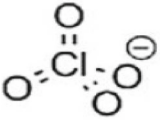
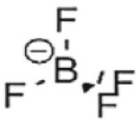
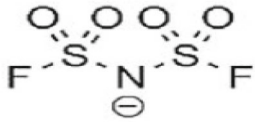
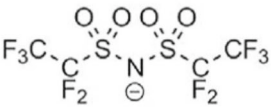
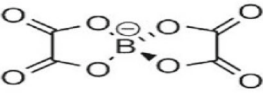
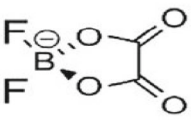
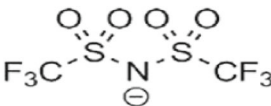
Lithium salt (abbreviations)	Anion	Main characteristics
LiClO ₄		➤ Broad electrochemical stability window ➤ Low solubility in commonly used carbonate-type solvents
LiBF ₄		➤ Broad electrochemical stability window ➤ Low solubility in commonly used carbonate-type solvents
LiPF ₆		➤ High ionic conductivity, favors SEI formation, passivates Al substrate at the cathode side ➤ Decomposes in the presence of moisture and reacts with electrolytes at elevated temperatures resulting in the formation of HF
LiFSI		➤ Higher ionic conductivity compared to LiTFSI, High electrochemical stability ➤ Unable to form passivation layers on Al current collectors (in the presence of LiCl) But purified LiCl free salt passivates Al collectors
LiBETI		➤ High solubility and high ionic conductivity, High electrochemical stability ➤ Unable to form passivation layers on Al current collectors
LiBOB		➤ High electrochemical stability and long term stability ➤ Form highly resistive SEI-films (low conductivity in comparison to LiPF₆ and LiTFSI)
LiDFOB		➤ High electrochemical stability and cycling behavior, Able to form passivation layer on Al current collectors ➤ Lower solubility in carbonate type solvents compared to LiTFSI and LiPF₆, but higher than LiBOB
LiTFSI		➤ High solubility and high ionic conductivity, High electrochemical stability ➤ Unable to form passivation layers on Al current collectors (Al-degradation and corrosion)

Table 8 Summary of the main effects of each class of filler within a polymer matrix (reprinted with permission from [125], copyright Elsevier 2014)

Filler class	Main effects in the polymeric matrix
Inert ceramic oxides	Higher ionic conductivity Increases discharge capacity Reinforces mechanical integrity
Ferroelectric material	Higher ionic conductivity
Super acid oxides	Higher ionic conductivity Enhances electrochemical stability
Clays	Higher ionic conductivity Improves thermal stability Improves electrolyte uptake
Carbonaceous fillers	Improves electrodes interfacial stability Enhances thermal stability
Molecular sieves and zeolites	Higher ionic conductivity Higher electrolyte uptake Better cycling performance
Lithium fillers	Improves electrochemical cell performance Enhances electrodes interface

is to use both cyclic and linear carbonates for desired organic solvent with improved properties such as ionic conductivity [131].

Sample preparation and methodology

Film preparation technique

With the increase of application of polymer electrolytes in many areas, it becomes necessary to find the preparation technique for high-quality film formation. Currently, polymer electrolyte membranes can be prepared by various methods such as, solution cast technique, tape-casting technique, in situ polymerization technique, melt intercalation technique, spin-coating technique, hot press technique, and dip-coating technique; some of the commonly used preparation techniques are given below.

Solution cast technique

It is a traditional method used due to its ease of fabrication which makes solid polymer electrolytes flexible (Fig. 4). It can produce polymer film from various thicknesses (50–300 μm). This process includes the following steps:

1. Addition of a specified amount of polymer to a solvent and kept for stirring for homogenous mixing.

2. The addition of salt in the polymer matrix and again stirred at room temperature till the polymer–salt complexation is formed.
3. After this, addition of nanofiller/clay/plasticizer is done and the stirring is done.
4. The viscous solution obtained is casted on glass or Teflon Petri dishes, and slow evaporation is done by keeping at room temperature for few days.
5. A thin film of uniform thickness is obtained.

In the solution cast technique, the solvent must be free from water content and should be a universal solvent which can dissolve both salt and the polymer [132]. The process of preparation of film is lengthy and long. It may take a long time (10–15 days) to get a complete dry film and also expensive in chemical use. Organic solvents such as DMF, acetonitrile (ACN), tetrahydrofuran (THF), and propylene carbonate (PC). It is a good method for preparing ionic salts (Li^+ , Na^+ , etc.) and proton-conducting system but fails for metal salts (Ag^+ , Cu^+ , Fe^+ , etc.).

Spin coating

The spin-coating method is almost the same as the solution casting method. Here, instead of casting the film on a substrate, the small amount of mixture is dropped on a substrate and placed in a spin coater which can be rotated at a desired rotation speed for a good film (Fig. 5). Substrate spinning axis must be perpendicular to the substrate which is to be coated. Centripetal acceleration will spread the mixture on the substrate. Then after, spread heating is done for evaporation of the solvent. The merits of the spin coating are the simplicity and relative ease of preparation and the ability to quickly produce uniform films from a few nanometers to a few microns in thickness. The film thickness can be controlled easily by adjusting the viscosity (concentration) of the mixture, surface tension, spin time, and the speed of rotation. The speed of rotation is an important parameter among them as it directly affects the force applied to the mixture. However, this method is advantageous only for low viscosity mixture not for too high viscosity mixture. For a gel mixture, the spin coater rotation is not enough to spread the mixture droplet to form a thin film [133–135].

Hot press technique

In place of the traditional solution cast technique, hot press technique is a novel technique due to its advantages such as quick method, low cost, solvent free, and may be used for dense materials. One advantage of this method is that a lot of alkali salts and metallic particles can be complexed with

Table 9 Properties of PE solvents for lithium battery systems

Serial no.	Abbreviation	Solvents	Molecular weight (g/mol)	Boiling point (°C)	Dielectric constant (at 25 °C)	Viscosity (cP)	Dipole moment (Debye)	Density (g/cm ³)
1	ACN (C ₂ H ₃ N)	Acetonitrile	41.05	81.6	35.95	0.341	3.92	0.377
2	THF (C ₄ H ₈ O)	Tetrahydrofuran	72.11	66	7.39	0.46	1.63	0.880
3	DMF (C ₃ H ₇ NO)	Dimethylformamide	73.10	158	36.71	0.796	3.82	0.944
4	DMSO (C ₂ H ₆ OS)	Dimethyl sulfoxide	78.13	189	46.45	1.991	3.96	1.095
5	DMC (C ₃ H ₆ O ₃)	Dimethyl carbonate	90.08	90.01	3.1	0.59	0.91	1.07
6	EC (C ₃ H ₄ O ₃)	Ethylene carbonate	88.06	248	89.6	1.85	4.9	1.322
7	PC (C ₄ H ₆ O ₃)	Propylene carbonate	102.1	241	64.4	2.53	4.9	1.19
8	DME (C ₄ H ₁₀ O ₂)	Dimethoxyethane	90.12	84.0	7.20	0.455	1.30	0.859
9	MF (C ₂ H ₄ O ₂)	Methyl formate	60.06	31.5	8.5	0.333	1.77	0.974
10	NM	Nitromethane	61.04	101.2	35.94	0.694	3.46	1.131
11	DEC (C ₅ H ₁₀ O ₃)	Diethyl carbonate	118.13	126	2.82	0.75	0.9	0.975
12	NMP (C ₅ H ₉ NO)	N-methyl-2-pyrrolidone	99.13	202–204	32.55	1.65	4.1	1.03
13	Toluene (C ₇ H ₈)	Toluene	92.14	111	2.38	0.590	0.31	0.865
14	H ₂ O	Water	18.01	100	80.1	0.890	1.87	1
15	C ₂ H ₆ O	Ethanol	46.06	78	24.5	1.26	1.69	0.789
16	C ₃ H ₆ O	Acetone	58.08	56	20.7	0.316	2.88	0.785
17	C ₃ H ₈ O	Isopropyl alcohol	60.1	82.6	19.92	1.96	1.66	0.786
18	CH ₃ OH	Methanol	32.04	64.7	33	0.79	1.70	0.791
19	C ₂ H ₆ O	Ethyl alcohol	46.06	78.37	24.55	1.095	1.66	0.789
20	C ₄ H ₈ O ₂	Ethyl acetate	88.11	78	6.02	0.45	1.88	0.894

various polymer hosts. The equipment consists of (a) weighing cylinder, (b) heating chamber, (c) basement, and (d) temperature controller. A dry powder mixture of optimized amounts of polymer, salt, and filler/plasticizer is grounded thoroughly at room temperature for 1–2 h in agate pestle and mortar. The physically blended mixture is heated slowly near the melting point of polymer in a heating chamber, and slurry obtained is then sandwiched under pressure between two stainless steel blocks. The sample is then pressed with a pressure controlled by a weighing cylinder [136]. It results in a hot slurry of different compositions of the polymer, salt, and filler which is separated from stainless steel (SS) blocks for further use (Fig. 6). The hot press technique is complicated for lithium ions due to reactive nature of lithium salts in the atmosphere and unique processing conditions are required [137–139].

Tape-casting technique

In this method, stoichiometric amounts of host polymer + salt are dissolved in a suitable solvent such as acetonitrile, DMF in a beaker, and solution is stirred for 10–12 h. Now, dispersion of nanofiller in different weight percent with respect to host polymer is done in the polymer–salt complex in the desired ratio and again stirring is done for the same time as above. Now, the resulting viscous solution is transferred on preheated hot plate for small time duration and cast by a tape caster with further drying slowly at room temperature. Thus, we obtain the free-standing conductive polymer nanocomposite film of desired thickness. The whole process is done in an inert atmosphere such as glove box (Fig. 7). A stainless steel container with slurry is connected to a gas steel chamber. The slurry flow rate

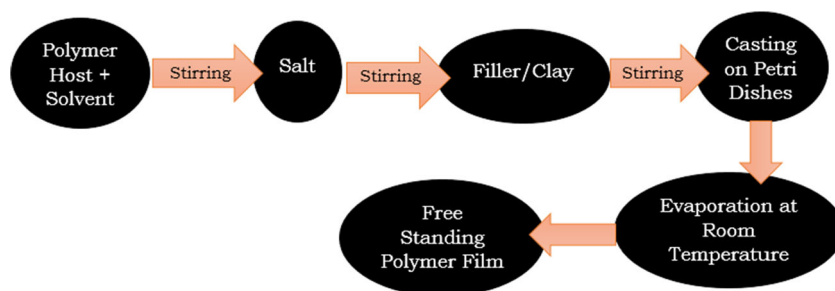
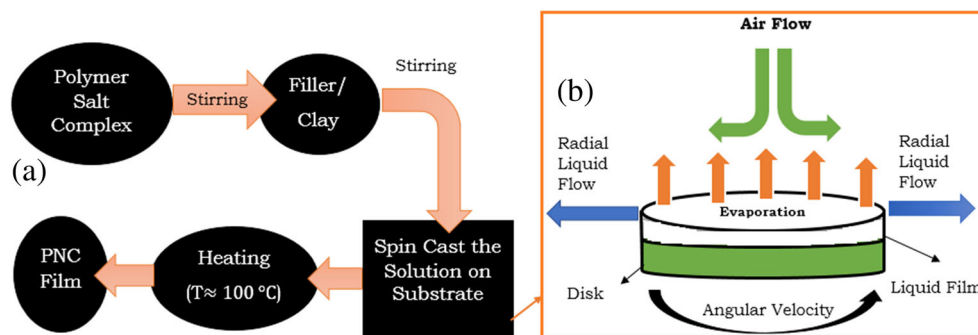
Fig. 4 Flow chart of solution cast technique

Fig. 5 **a** Flow chart of spin-coating technique. **b** Schematic illustration of the spin coating



is controlled by the gas pressure and amount of slurry at scraper edge is kept constant [140]. When a carrier (tape) is passed through a slurry at a fixed rate, there is a slit between the edge of the scraper and the carrier. When the slurry on the carrier with the thickness of the slit is dried, a membrane is obtained and rolled into a package. The slit can be adjusted to prepare membranes with varied thickness. Both thickness and width of the film can be easily controlled by this technique and suitable for production at industrial scale [141].

Screen printing

This technique is simple to operate and produces a film of uniform thickness on different substrates. In this method, a polymer solution or slurry is spread on dense net whose bottom is attached to a smooth metal plate as a carrier. Now, a squeezer is passed over the slurry with some force, causing the slurry to flow through the net (mesh) and form a uniform thin membrane in metal plate carrier. After drying, the thin film is taken off from the carrier. Figure 8 shows the screen printing technique for the silver paste coating on substrate [142]. The thickness of film depends on the solution viscosity, mesh diameter of the net, applied force on squeezer, and the velocity of squeezer on the metal plate. So, the above process is good with only one limitation that thickness is not easily controlled.

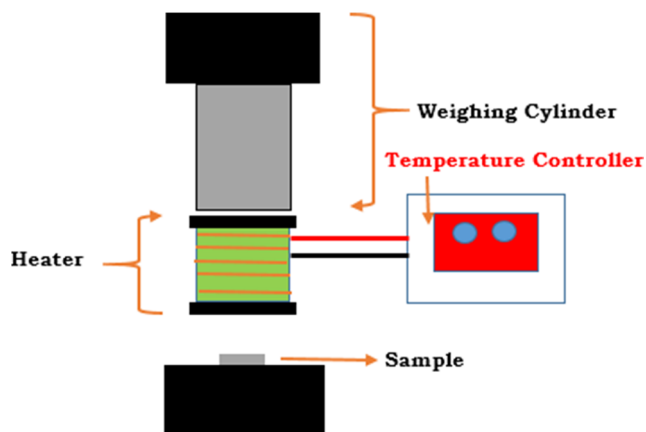


Fig. 6 Schematic diagram of hot press technique

Dip coating

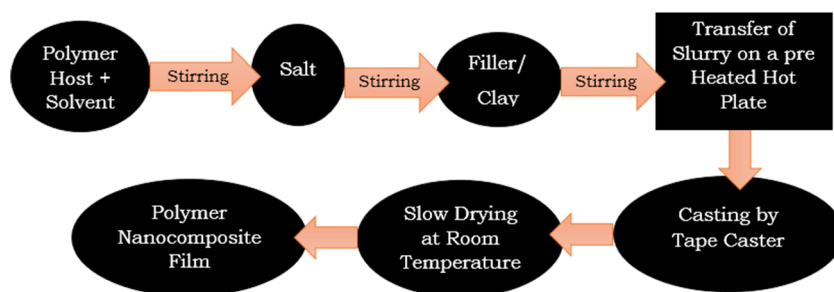
Dip coating is the frequently used process at industry level due to its simplicity, low cost, and that a high-quality film on both sides of the substrate can be obtained. In this process, the substrate is dipped into the solvent of which coating is to be done and uses a small amount of liquid than spin-coating technique [143]. It is a three-step process as shown in Fig. 9.

1. Immersion: the substrate is immersed in the precursor solution of the coating material at a constant speed (preferably jitter free).
2. Deposition and drainage: the substrate has remained inside the solution for sufficient interaction of the substrate with the solvent called dwell time and is starting to be pulled up when the solution is in the rest state. The thin layer gets deposited on the substrate and is pulled up at a constant speed leading to thin film formation. Extra liquid will drain from surfaces while removing the substrate up. The film thickness is easily controlled by pulling speed and density of particles.
3. Evaporation: the solvent evaporates from the solvent, and a thin film is deposited after drying it. Further drying can be done to remove the residual solvent.

Melt intercalation technique

Melt intercalation technique is a standard for the preparation of polymer nanocomposite due to its advantages such as being environmentally friendly, absence of solvent, and low cost (Fig. 10). It involves annealing the polymer matrix at high temperatures, adding the filler, and finally kneading the composite to achieve a uniform distribution. One limitation is that high temperature may damage the surface properties of nanofiller via degradation. So, optimization of thermal properties is important to obtain better dispersion of nanofiller in the polymer matrix. This technique is better than solution cast method due to its lack of solvent. However, processing conditions and surface modification of clay/nanofiller

Fig. 7 Tape-casting technique flow chart



compatibility of filler with host polymer play a key role in the dispersion of filler [144, 145].

Characterization technique

The characterization of PEs is done using various techniques. These techniques give analysis of surface, microstructural, structural, interaction in complex, thermal parameters, electrical conductivity, ionic transference number, and potential stability window.

A snapshot of the characterization technique and the information obtained are presented in a tabular form in Table 10.

Results, discussion, and analysis

Structural and microstructural property analysis

X-ray diffraction

X-ray diffraction pattern is a versatile, non-destructive analytical technique for the identification of phases and amorphous content of the sample. Thakur et al. [146] prepared a nanocomposite electrolyte based on PEO- NaClO_4 with *Nanmontmorillonite* (MMT) as clay using tape cast technique and studied the effect on structural and microstructural properties. X-ray diffraction (XRD) results suggest a strong interaction between polymer–salt complex and clay networks with certain evidence of the polymer–salt complex interplay with

nanometric clay channels. It has also been observed that the d_{001} value increases for low concentration of clay followed by a decrease in higher clay concentration. XRD spectra show better dissolution of salt in PAN polymer host, and presence of the sharp peak at high salt concentration shows cluster formation [147]. XRD spectra display some additional peaks on the addition of salt in polymer host [148]. XRD spectra show peak broadening with the addition of salt and confirm the complex formation of the salt with polymer host [149]. XRD spectra show disappearance of peaks for NaF at 39° and 56° , for polymer blend complex, and the multiphase system was confirmed having both crystalline and the amorphous region. After addition of salt, the crystalline region is disrupted, and peak broadening is seen with a decrease in intensity [150]. XRD spectra show no peak corresponding to salt due to complexation with polymer host. It also provides the information that crystallinity of PAN does not change with addition of nanowires [151]. XRD spectra show shift and decrease in the relative intensity of the peaks due to complexation between polymer and salt. The blending of PEMA with PVC also reduces intensity more because of redistribution of orders arrangement o polymer. There was no peak for the Li salt and is evidence of the presence of amorphous phase in SPE [152].

Mohapatra et al. [153] reported the effect of filler SnO_2 on morphological, electrical, electrochemical, and mechanical stabilities of the CPE film with PEO as host polymer and NaI as salt. XRD and SEM studies extract the structural and morphological properties of polymer nanocomposite film (Fig. 11). XRD pattern shows two major peaks of PAN at

Fig. 8 A schematic diagram of a screen printing device utilized for commercial production of front-side silver conductive lines (reprinted with permission from [142], copyright Springer 2013)

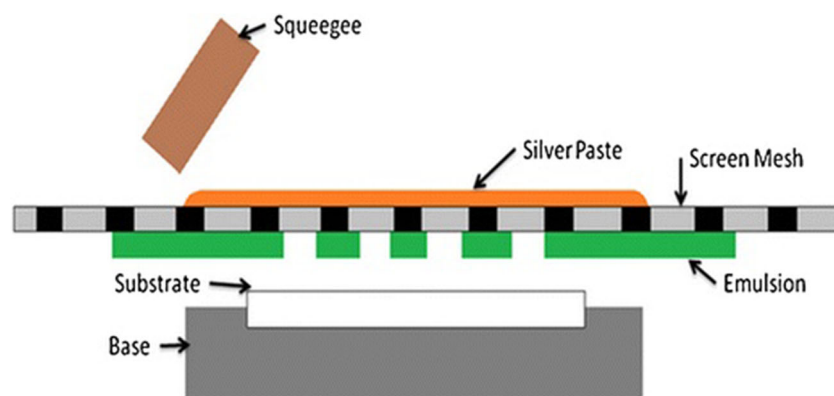
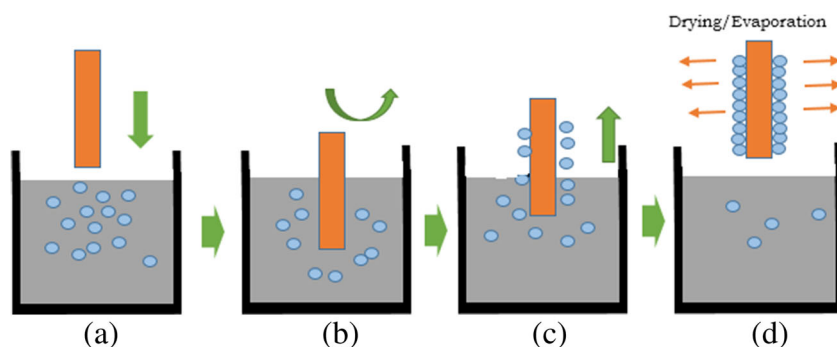


Fig. 9 Stages of dip-coating process. **a** Immersion. **b** Deposition. **c** Drainage. **d** Evaporation of solvent



$2\theta \sim 14.2^\circ$, 22.4° with Miller indices [010] and [300], and absence of LiPF_6 peak confirms the complex formation. After incorporation of clay in PS complex, PAN peak profile shows variation regarding the change in the peak intensity, d -spacing, and polymer interchain separation. The drastic changes in the d_{001} peak pattern of the clay observed at $2\theta \sim 5.8^\circ$ confirms the strong interaction between polymer host and DMMT clay in PNC film [83]. XRD pattern confirms presence of the amorphous region in pure PAN and leads to more polymer flexibility and greater ionic diffusivity [154]. XRD spectra show the presence of a single laminar phase for both molecular weight SPE and absence of pure PEO peak ($2\theta = 15^\circ$ and 30°) is evidence of the existence of amorphous phase. For composite electrolyte diffraction peak at $2\theta = 5.16^\circ$, spontaneous intercalation of polymer into clay [155] is shown. XRD spectra show a broad peak of poly(vinyl alcohol) (PVA) between 17° and 22° corresponding to (110) reflection and is associated with the amorphous phase of the polymer matrix. The absence of peaks corresponding to magnesium nitrate salt evidences the complete dissolution of salt in polymer host [75]. XRD pattern suggests the presence of amorphous region. The shift of XRD peak towards the higher angle side results due to the increase in d -spacing of the polymer matrix, indicating evidence of the interaction of salt with PMMA and arising out of a possible complexation of cation (Li^+ ion) with the electron-rich site in the host polymer matrix [156]. XRD patterns show the highly crystalline system with relatively sharp diffraction peaks [157]. Leo et al. [158] prepared composite polymer electrolyte based on PEO + Li triflate with Li Nasicomponent ($\text{Li}_{1.4}(\text{Al}_{0.4}\text{Ge}_{1.6})(\text{PO}_4)_3$) as the ceramic filler

and EC + PC as the plasticizer. XRD spectra show the decrease in intensity with the addition of filler as observed decrease in intensity and broadening in the area of the peak. The increase in background noise indicates the enhancement in the amorphous phase.

XRD pattern shows the absence of peaks corresponding to pure Li salt and the diminished crystalline region is obtained. Further analysis showed the absence of PVC peak at $2\theta = 13^\circ$ and structural modification is observed. The shifting and decrease in intensity of PEMA peak are evidence of a good complex formation between polymer blend and salt [159]. Sengwa et al. [160] prepared the polymer blend-based electrolyte films based on PEO-PMMA + LiCF_3SO_3 ($(\text{EO} + (\text{C} = \text{O}))\text{-Li}^+ = 9:1$) as a dopant ionic salt and PEG as plasticizer by different methods such as solution cast melt pressed/ultrasonic assisted followed by microwave-irradiated solution cast melt-pressed methods. PMMA was used as a blend due to light weight with high transparency, high strength, and dimensional stability. XRD spectra confirm the complete dissociation of salt and formation of ion dipolar complex change the polymer blend into the amorphous matrix. US-MW-prepared films show less peak intensity, suggesting the decrease in the crystalline region with the addition of nanofiller.

Transmission electron microscopy (TEM)

It provides the direct microstructural information of sample by cross section and in plane view. It provides a high-resolution image and select area diffraction pattern (SAED) with digital facilities. So, it helps us to find out the mechanism of film

Fig. 10 Flow chart of melt intercalation technique

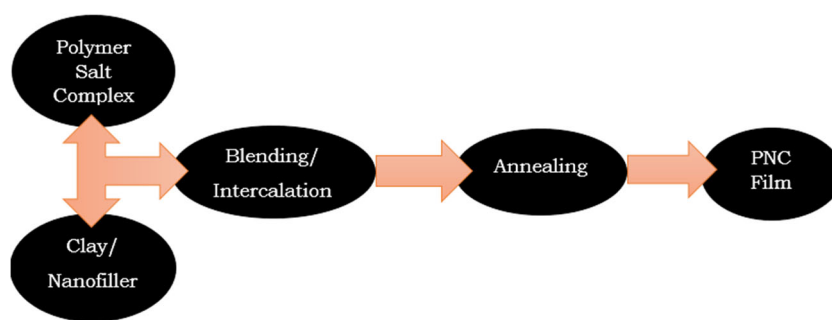


Table 10 Some common characterization techniques and information obtained for PEs

Serial no.	Techniques	Information obtained
1	X-ray diffraction (XRD)	(i) To conform composite formation. To understand the polymer–salt and filler/clay interaction. (ii) To estimate nature of interaction and structure changes. (iii) To calculate crystallinity, crystalline size, Scherer length, and interchain separation. (iv) To confirm intercalation, dispersion or exfoliation of polymer nanocomposite.
2	Transmission electron microscopy (TEM)	(i) To investigate crystal structure, orientation and chemical composition in phases, precipitates, and contaminates. (ii) Qualitative and quantitative analysis can be provided from the texture less than 30 nm. (iii) It is used to determine the atomic arrangement of single crystal. (iv) It is used to determine the structural examination like: defect sites, precipitates, and vacancies in the crystal of the materials.
3	Atomic force microscopy (AFM)	It helps to investigate the surface morphology along with dimensional stability (mechanical analysis).
4	Fourier transform infrared spectroscopy (FTIR)	(i) To probe the ion association and dissociation, free anion, ion pair and ion aggregates present in the matrix of the sample. (ii) To determine the functional group present in the matrix.
5	Differential scanning calorimetry (DSC)	It gives the thermodynamic properties like (glass transition (T_g), phase changes, melting (T_m), crystallization (T_c), product stability, cure kinetics, and oxidative stability).
6	Impedance spectroscopy (IS)	It determines the different phases present in the sample. It helps to determine the conductivity, impedance, and activation energy of the composites.
7	Transference number (t_{ion})	To probe that PNCs matrix are ionic conductor.
8	Linear sweep voltammetry (LSV)	To determine the electrochemical stability window of the PNCs sample.
9	Thermogravimetric analysis (TGA)	It mainly gives the matrix thermal stability and material composition.
10	Dynamic mechanical analysis (DMA)	It helps to determine the mechanical properties of the sample.
11	Chronopotentiometry (CP)	To determine the capacity and energy density of cell using PNCs.
12	Cyclic voltammetry (CV)	To study the voltage stability of PNCs.

growth and design of thin film-based devices. Sharma et al. [83] observed the surface property and morphological features of the PNC films (Fig. 12 (I)). The dark slices in the transmission electron microscopy (TEM) graph suggest the presence of exfoliation of the PS matrix in the PNC at low clay loading

due to the presence of individual clay platelets dispersed homogeneously in the PS matrix. While at high clay loading, presence of well-defined stacks representing clay channels with PS is clearly visible (Fig. 12 (I (c))). The SAED pattern confirms that the crystalline nature of the PNC films has

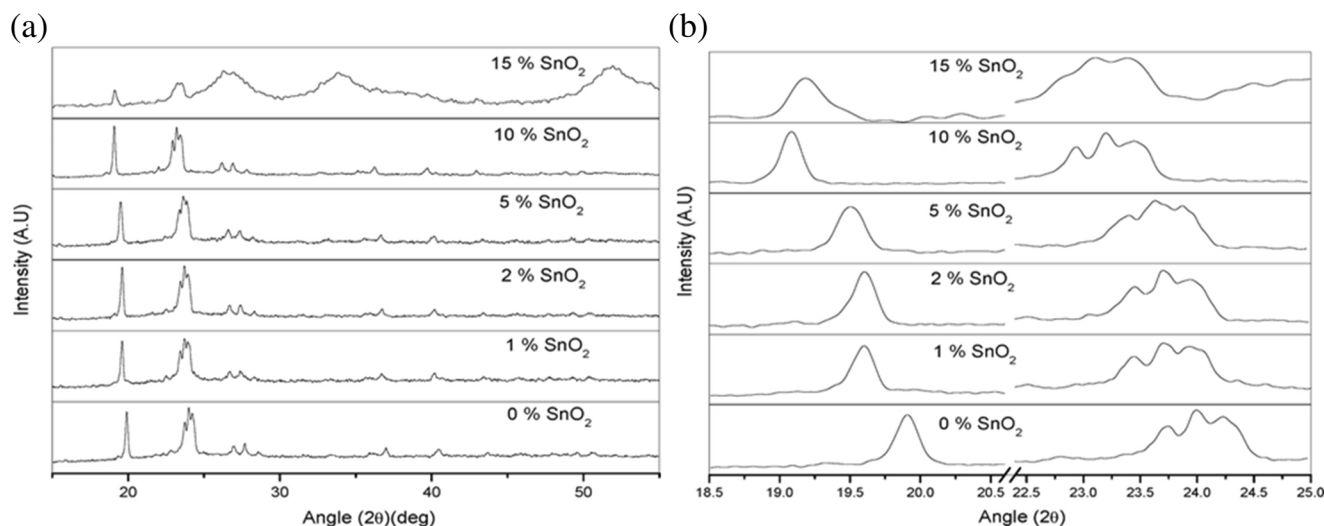


Fig. 11 **a** XRD pattern of $\text{PEO}_{25}\text{-NaI} + x \text{ wt\% SnO}_2$ films ($x = 0, 1, 2, 5, 10$, and 15). **b** Effect of filler on changes in PEO diffraction peaks in $\text{PEO}_{25}\text{-NaI} + x \text{ wt\% SnO}_2$ films ($x = 0, 1, 2, 5, 10$, and 15) (Reprinted with permission from [153], copyright Springer 2007)

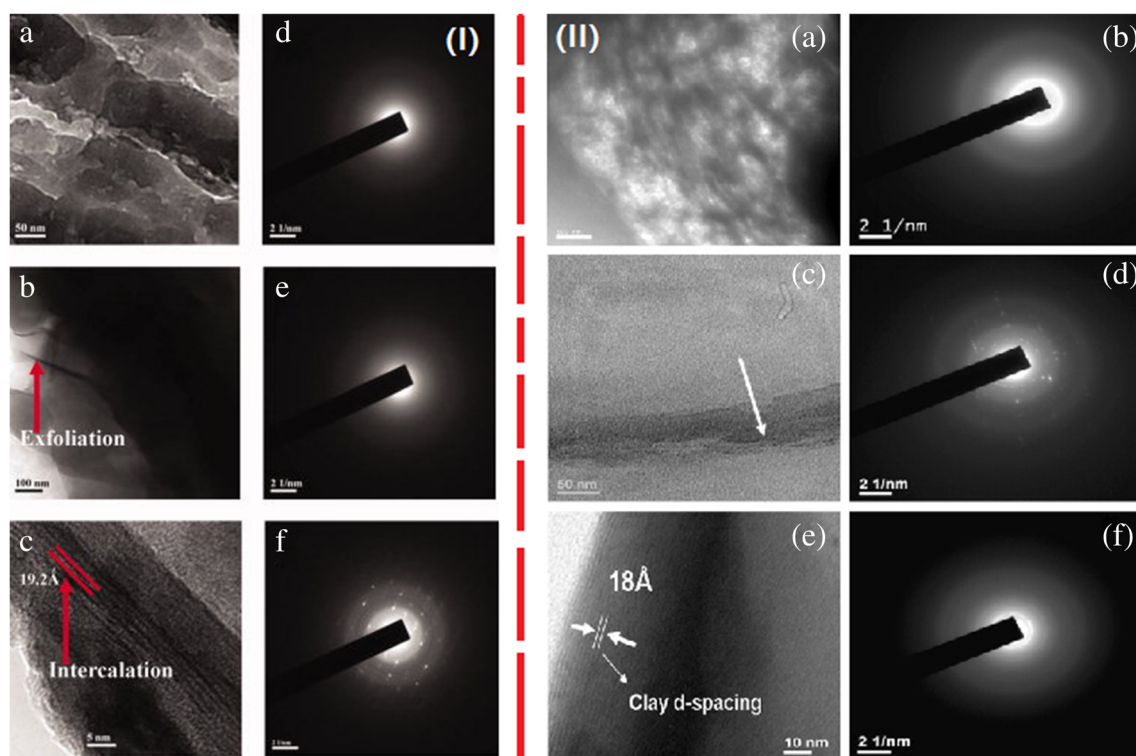


Fig. 12 I TEM and selected area electron diffraction (SAED) pattern of PNC films at organo-modified clay concentration ($x = 0\%$, 2% , and 15%) (Reprinted with permission from [83], copyright Springer 2013). II TEM micrograph of PS, 5 and 20 wt.% DMMT-dispersed PNCs in (a), (c), and

(e), respectively. SAED patterns are given sequentially in (b), (d), and (f) next to corresponding image patterns (reprinted with permission from [161], copyright Elsevier 2009)

improved on nanocomposite formation and dominated with an increase in clay concentration (Fig. 12 (I (d–f))). Another study of TEM analysis of PEO-LiClO₄ + MMT clay has been reported to observe the change in surface property/morphology on intercalation of PS into the nanometric clay channels as shown in Fig. 12 (II) [161]. Polymer matrix without clay shows the multiphase character as in Fig. 12 (II (a)) and the SAED pattern of polymer–salt matrix shows well-defined rings at the centre followed by hollow region thereafter. The dispersion depends on the nature of the interaction between the polymer salt and clay. The degree of dispersion of the clay particulates into the PS matrix controls the structure and morphological features of the composite nanostructures as observed in terms of change in surface morphology after addition of clay.

TEM observes the evidence of the clay concentration-dependent interaction among the components (PS and clay) in the PNC films. At low clay loading, the individual-layered silicates appear to be dispersed randomly in the PS matrix to field an exfoliated structure in the nanocomposite and alignment of silicate layers is observed (marked with an arrow) (Fig. 12 (II) (c)). With the increase in clay concentration, coherent stacking of silicate layers separated by ~ 1 nm occurs due to the entry of cation-coordinated polymer chain in clay channels where dark lines are silicate layers of the organo-modified clay reinforced with PS matrix. The following

micrographs (Fig. 12 (II) (e)) clearly reveal the topography of the intercalated PNC film with an enlarged clay gallery width ~ 18 Å for 20 wt.% loading of DMMT clay. Liu et al. [151] reported the enhancement in conductivity value after addition of ceramic nanowire fillers in PAN-LiClO₄ system, and TEM images of SPEs shows that nanowires are fully embedded into polymer host.

Atomic force microscopy

It is a most versatile and powerful 3D technique to study the samples at the nanoscale. Atomic force microscope (AFM) micrographs show changes in the surface topography and phase in the PNC films for various filler concentration and near surface nanostructure is formed (Fig. 13). The 3D image shows the humps evidencing the atomic corrugation at the nanoscale while color pattern confirms the presence of multiphase composite type behavior after clay intercalation [146].

Fourier transform infrared analysis

Fourier transform infrared spectroscopy (FTIR) shows the [162] various constituent groups of composite polymer films and feasibility of clay in polymer–salt complex. The significant stretching and deformational mode of PAN change on addition of clay (Fig. 14 (I)). The PAN skeletal group

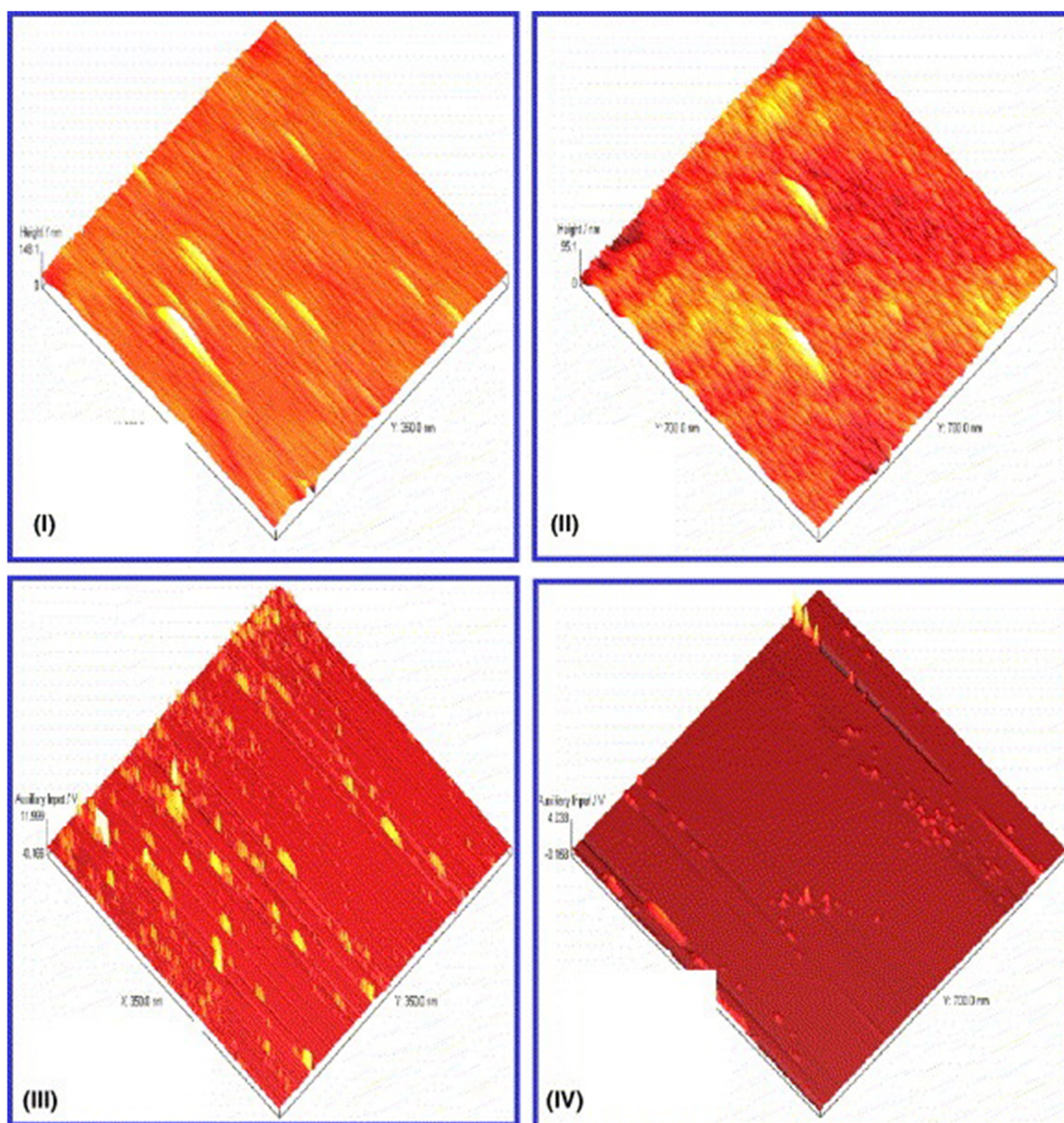
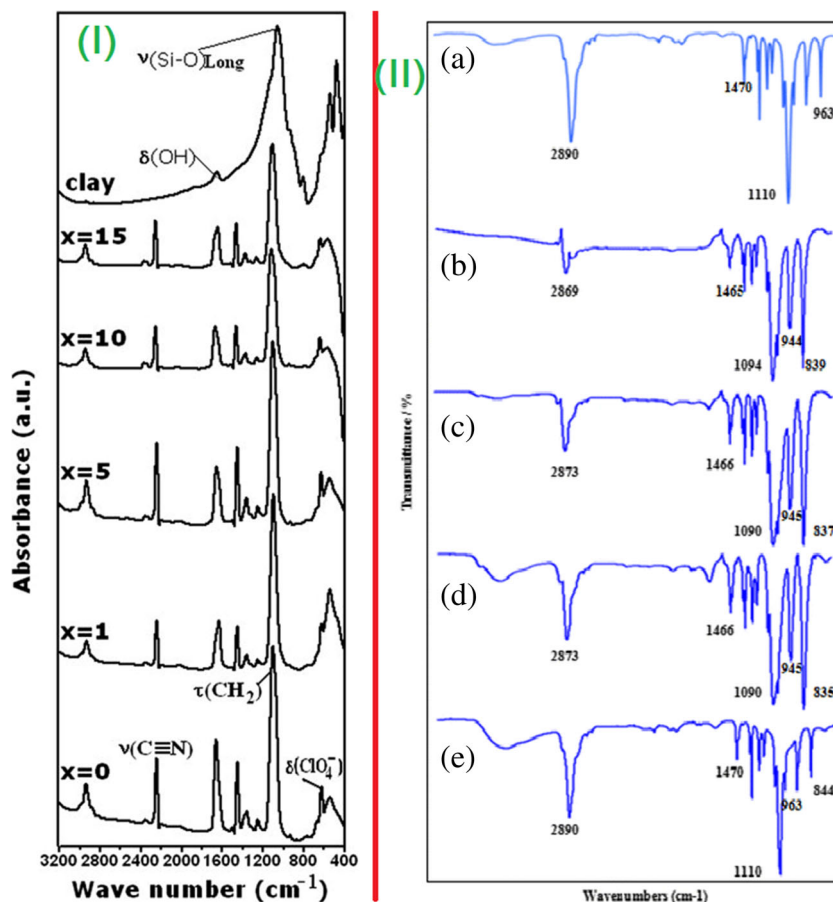


Fig. 13 AFM micrographs of PNC films showing, topography for $x = 0\%$ (i) and $x = 5\%$ clay concentration (ii) and phase image for $x = 0\%$ (iii) and $x = 10\%$ clay concentration (iv) (reprinted with permission from [146], copyright Elsevier 2006)

vibrational mode shifts upward and evidence the interaction of salt with the polymer PAN matrix. The absence of salt interaction with the solvent skeletal group (i.e., CH_3 , $\text{C}-\text{CH}_3$, and $\text{C}-\text{N}$) concludes that an efficient interaction of salt occurs with ($-\text{C}\equiv\text{N}$) of the host polymer which is an active site for coordination with Li^+ ion in the polymer backbone. The CH_2 scissoring mode profile changes on addition of clay and shows regarding changes in the intensity and width of shoulder observed at 1420 cm^{-1} with increasing clay concentration. The band corresponding to stretching vibration mode of $\text{Si}-\text{O}$ in the silicate layer is observed at 1041 cm^{-1} and get masked possibly due to overlapping of the $\text{m}(\text{Si}-\text{O})$ band of the clay and $\text{s}(\text{CH}_2)$ band of the PAN in the PNC films. Another study of $\text{PEO}-\text{LiPF}_6$ -based polymer electrolyte done by Ibrahim

et al. [188] which shows the peak broadening with an increase in LiPF_6 salt concentration and may be assigned to the decomposition of LiPF_6 to solid LiF and gases of OPF_3 and HF . The increase in salt concentration shows the increase in intensity and shifting of symmetric stretching vibration band of pure PEO and may be due to an additional amount of Li^+ in the complexes. Peak broadening is observed in all samples except 20 wt.% PS film due to the formation of ion pairs/triplets which restricts the ion segmental motion and polymer flexibility (Fig. 14 (II)). Mohapatra et al. [163] studied the FTIR spectra of $\text{PEO}_8-\text{LiClO}_4 - x$ (wt.%) nano- CeO_2 -based PNC and showed the role of nanoceramic filler on ion-ion and ion-polymer interactions. Detailed analysis of pattern displays change in vibrational bands/profile in PNC films and shows

Fig. 14 I Fourier transform infrared (FTIR) spectrum of PNC films; $(\text{PAN})_8\text{LiClO}_4 + x$ (wt.%) Montmorillonite (MMT) in the wavenumber region 400 to 3200 cm^{-1} (Reprinted with permission from [162]). II FTIR spectra of pure PEO and various weight percents of LiPF_6 in complexes a 0, b 5, c 10, d 15, and e 20 (reprinted with permission from [217], copyright Springer 2011)



an active role of filler in affecting polymer–ion and ion–ion interaction in the films. The spectral pattern of perchlorate (ClO_4^-) group in the wavenumber region $600\text{--}650\text{ cm}^{-1}$ is observed with the presence of asymmetry attributed to (ClO_4^-) vibrational mode with absorption maxima at $\sim 629\text{ cm}^{-1}$ may be attributed to coordination of anion with counter ions. So, the deconvolution is done to study the simultaneous presence of free ion–ion pairs in the PNC films using Peak-Fit software as shown in Fig. 15. It shows two distinct contributions: one at lower wavenumber side and one at higher wavenumber side due to peak asymmetry. For 2 wt.% filler, peak area for ion pair is less than free ion area and suggests the feasibility of a strong ion–filler interaction arising due to the strongly dipolar and acidic nature of the nano- CeO_2 having a high surface area (Table 11). This increase in free anion may be due to ion dissociation effect. At high filler loading, free anion area decreases due to ion aggregation.

Sharma et al. [13] studied the FTIR spectra based on $(\text{PAN})_8\text{-LiCF}_3\text{SO}_3$ with MMT as clay in wavenumber region $400\text{--}4000\text{ cm}^{-1}$. The changes in the deformation mode of CF_3 ($\delta_d(\text{CF}_3)$) of the CF_3SO_3^- of the salt (LiCF_3SO_3) with clay concentration in the PNC are detailed subsequently. The changes in the position, width, and symmetry of CF_3SO_3 band observed at the wavenumber 517 cm^{-1} is attributed to the

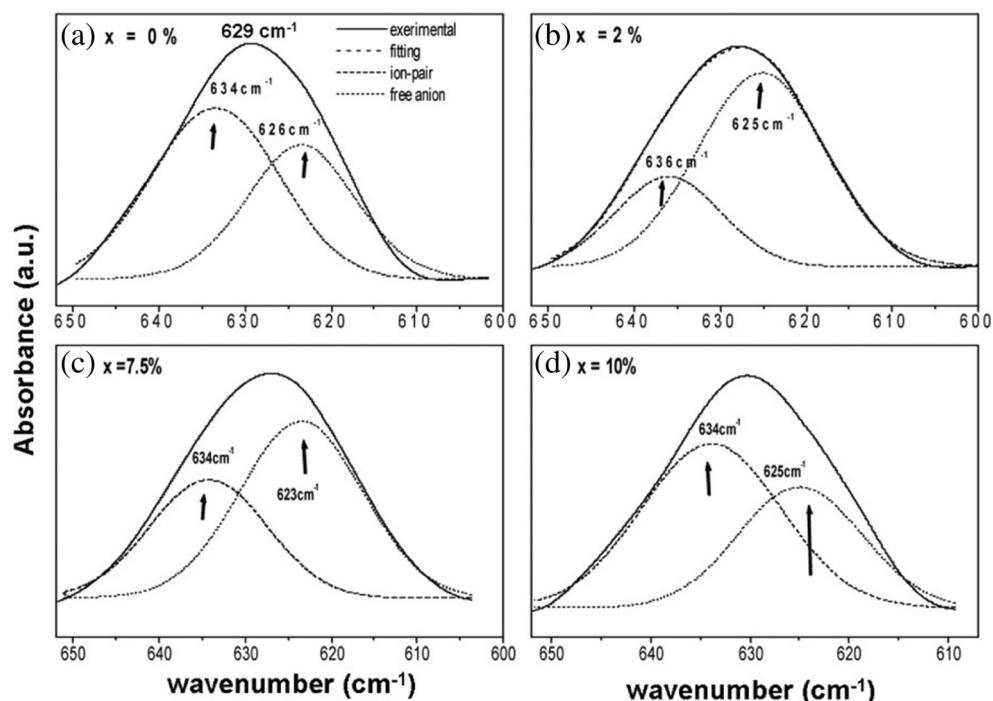
interaction of ionic species (basically Li^+) coordinated with the host polymer (PAN). The changes in the spectral pattern observed at wavenumbers ~ 1360 , 2245 , and $\sim 2940\text{ cm}^{-1}$ may directly be related to the interaction of polymer host matrix with organo-modified clay (DMMT). The asymmetry in the CF_3SO_3 mode was deconvoluted by Voigt profile and shows the presence of two contributions. The peak appearing at 512 cm^{-1} has been associated to the free anion, and peak appearing at 522 cm^{-1} corresponds to the presence of “ion pair” in the solid polymer clay matrix. The changes in the free anion area and ion pair area suggest the active role played by clay in interaction with polymer and polymer–salt matrix as shown in Fig. 16.

Impedance/electrical conductivity analysis

In this technique, a sinusoidal signal of low amplitude (10 mV) is applied across the sample by placing it between two electrodes. Impedance data is obtained in terms of real and imaginary parts of impedances called Nyquist plot.

Prasanth et al. [35] investigated the effect of PEO on electrochemical properties of electrospun PVdF-based PEs studied. The highest ionic conductivity value is $4.9 \times 10^{-3}\text{ S cm}^{-1}$ at room temperature for LiTFSI salt and confirms that the

Fig. 15 Typical deconvoluted pattern of perchlorate (ClO_4^-) band at 629 cm^{-1} showing profile of the individual contribution due to free anion and ion pair in the **a** PS and for $\text{PEO}_8\text{LiClO}_4 - x$ (wt.%) CeO_2 with **b** $x = 2$, **c** $x = 7.5$, and **d** $x = 10$ (reprinted with permission from [163], copyright Wiley 2009)



electrospun membrane-based GPE provides faster transport of ion. The complex impedance study was done for Li/PGE/Li symmetric cells and then repeated after 12 days storage measured at open circuit potential at ambient temperature. The presence of semicircle in middle-frequency range provides evidence of formation and growth of passivation layer at electrode/electrolyte interface (Fig. 17). The value of bulk resistance changes with the change in salt.

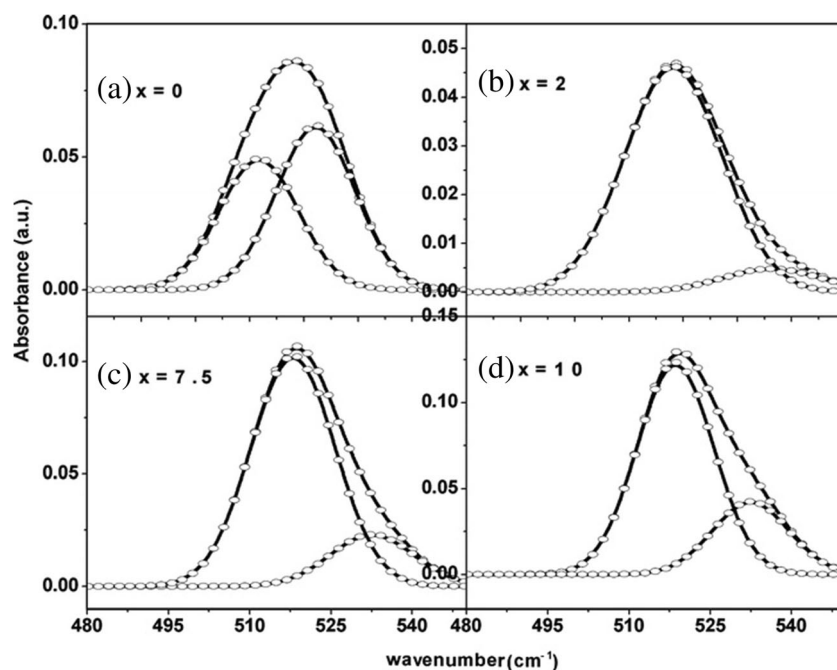
The highest ionic conductivity value obtained for PVC-PEO + LiCF_3SO_3 is at $3.3 \times 10^{-4}\text{ S cm}^{-1}$ with optimum concentration 5 wt.% of silica and is attributed to more disorder and enhanced amorphous nature due to Lewis acid nature and high surface area of nanofiller respectively of the silica. At higher silica content, decrease in conductivity may be due to increase in viscosity and crystalline region. The value for the activation energy of 1.0 eV was extracted from the gradient of conductivity vs. temperature curve [164]. The ionic conductivity increases from 2.5×10^{-3} to $3.5 \times 10^{-3}\text{ S cm}^{-1}$ after doping $\text{SiO}_2/\text{PAALi}$

ion complex; an ion transport occurs by the entrapped liquid electrolyte which enhances the amorphous content and prevents leakage of liquid electrolyte [83]. Li et al. [165] investigated the porous PVdF-HFP membrane with Al_2O_3 nanoparticles, and it was concluded that the crystallinity of polymer matrix decreases with Al_2O_3 nanoparticles due to their solid plasticization effect. The highest conductivity of $2.11 \times 10^{-3}\text{ S cm}^{-1}$, lithium cation transference number of 0.66, and the activation energy for ion transport of 4.816 kJ mol^{-1} was obtained for 10 wt.% of nanofiller. For $\text{Ö/Li} = 4$, salt dissolution into the PMMA matrix was highest due to the availability of highest number of free ions for transport within coordinating site [156]. The conductivity value of pure PMMA on complexation with salts increased from 10^{-16} to 10^{-7} S cm^{-1} at 30°C . The $\text{Ö/Li} = 2$ ratio shows the lower value of conductivity than $\text{Ö/Li} = 4$ because in the later concentration, complete dissolution of salt with polymer matrix provides two coordinating sites for cation in the PS matrix. Variation of conductivity obeys Vogel–Tamman–

Table 11 Quantitative estimates of the fraction of free anion and ion pair from deconvoluted ClO_4^- band profile of the $\text{PEO}_8\text{-LiClO}_4 + x$ (wt.%) nano- CeO_2 -based polymer nanocomposite films (reprinted with permission from [163])

Nano- CeO_2 concentration (wt.%)	Free anion peak (cm^{-1})	Ion-pair peak (cm^{-1})	Free anion area (%)	Ion-pair area (%)	Correlation coefficient (r^2)
0	626	634	59	41	0.995
1	626	637	74	26	0.999
2	625	636	73	27	0.999
5	626	637	76	24	0.999
7.5	623	633	62	38	0.997
10	625	634	39	61	0.995
15	621	631	32	68	0.996

Fig. 16 Ion–ion and ion–clay interactions indicated by deconvolution pattern of deformation mode of CF_3 of $(\text{PAN})_8\text{LiCF}_3\text{SO}_3 + x$ (wt.%) DMMT films (reprinted with permission from [13], copyright Springer 2009)



Fulcher (VTF)-type behavior according to which ionic conduction is dominated by segmental motion at high temperature and less internal friction enhances mobility or conductivity. The ionic conductivity of pure PVA is $5.9 \times 10^{-9} \text{ S cm}^{-1}$ and increases to $7.36 \times 10^{-7} \text{ S cm}^{-1}$ for 30 wt.% salt. Also, activation energy (E_a) decreased from 0.72 to 0.67 eV in addition to salt at 30 wt.% [157]. Yang et al. [50] studied a sodium ion-conducting gel polymer electrolyte based on PVdF-HFP. Ionic conductivity variation with temperature is shown in Fig. 18.

The effect of the presence of PEO-bentonite- Li^+ as filler in SPE with PEO 600,000, shows that a conductivity of

$1.81 \times 10^{-7} \text{ S cm}^{-1}$ is attained, i.e., an increase of about two orders of magnitude respect to pure PEO ($1.2 \times 10^{-9} \text{ S cm}^{-1}$) and more than five times that of bentonite- Li^+ . This increase in conductivity may be due to Lewis acid–base interaction, kinetics of charge carriers, and changes of crystallinity and segmental movements of the host polymer. Because of its higher affinity with PEO, this nanocomposite could reach more easily crystalline domains of the polymer, thus altering its structure and producing more favorable conditions for ionic transport of charge carriers with coordinating sites of the polymer

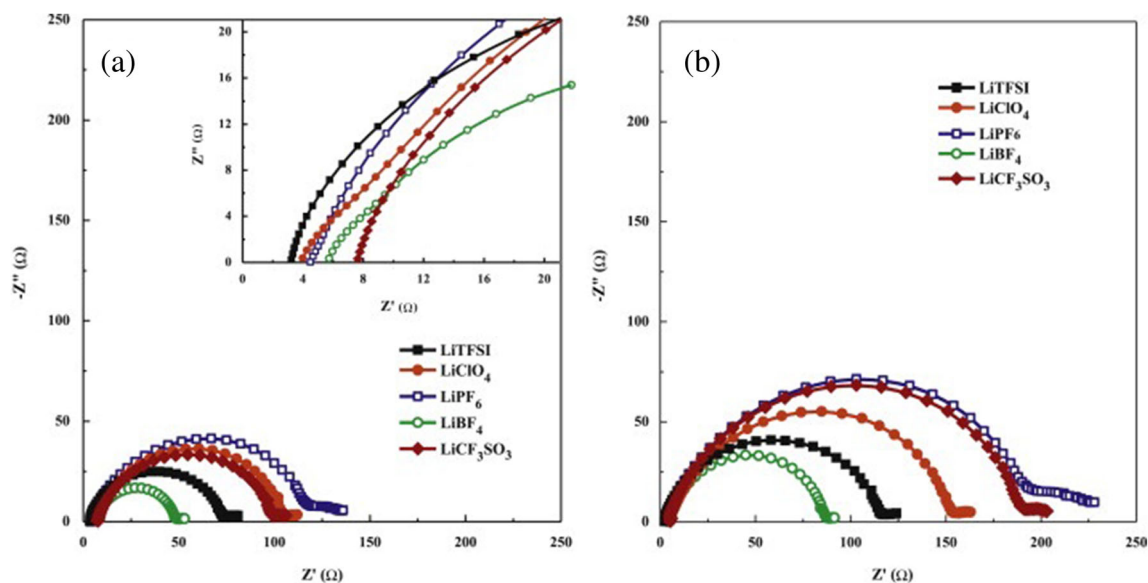


Fig. 17 AC impedance behaviors of polymer electrolytes based on electrospun PVdF/PEO polymer blend membranes (Li/PGE/Li cells, frequency range 10 mHz–1 MHz, amplitude 20 mV): **a** initial impedance and **b** impedance after 12 days of storage (reprinted from [35], copyright Elsevier 2014)

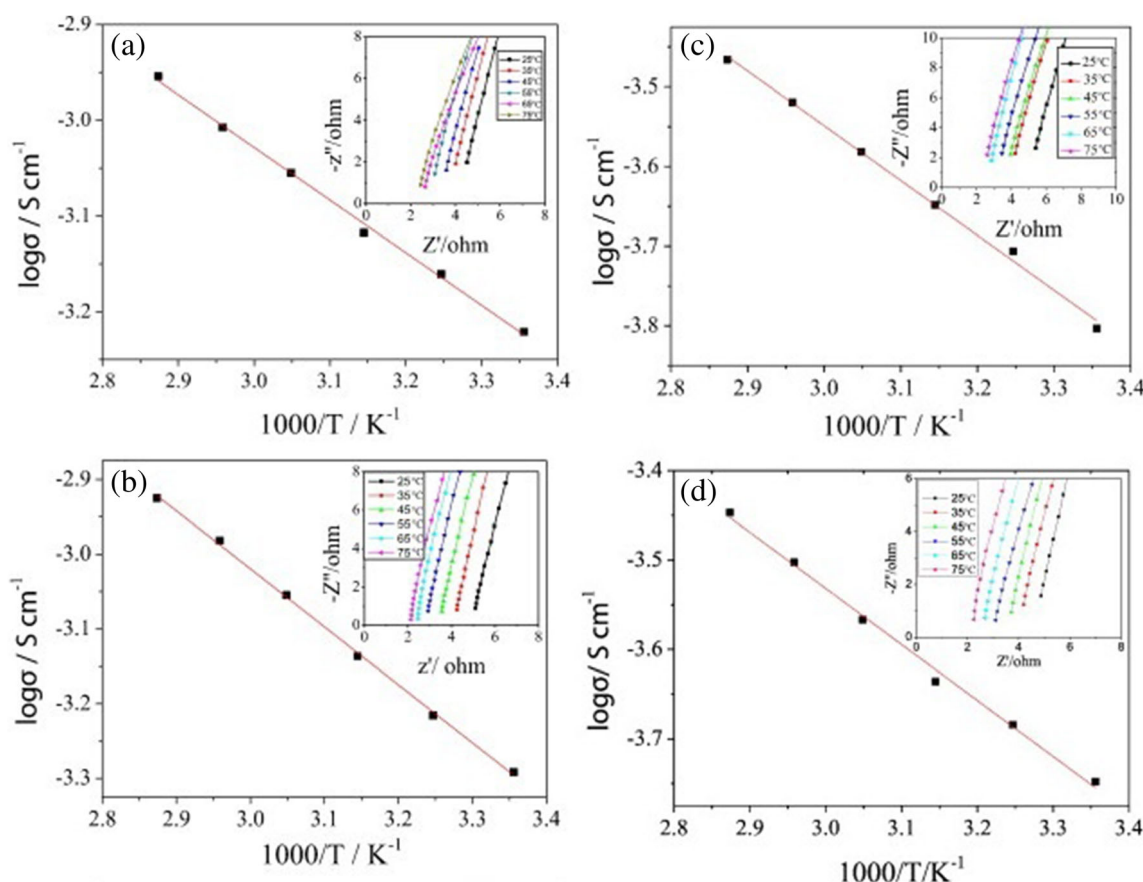


Fig. 18 Plots of log of ionic conductivity vs. $1000/T$ for **a** P(VDF-HFP) saturated with 1 M NaClO_4 organic electrolyte, **b** P(VDF-HFP) saturated with 1 M LiClO_4 organic electrolyte, **c** Celgard 2730 saturated with 1 M

NaClO_4 organic electrolyte, and **d** Celgard 2730 saturated with 1 M LiClO_4 organic electrolyte (reprinted with permission from [50], copyright Elsevier 2015)

[155]. The addition of nano- Al_2O_3 in PS complex further improves the conductivity and amorphous phase by reducing the crystallinity of SPE. The conductivity variation with temperature follows the Arrhenius behavior and activation energy decreased from $20.10 \text{ kJ mol}^{-1}$ (PS complex) to $10.96 \text{ kJ mol}^{-1}$ with the increase of the Al_2O_3 concentration. The ionic conductivity of PEO-PMMA-LiTFSI- Al_2O_3 electrolyte reaches $1.62 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature and $3.24 \times 10^{-4} \text{ S cm}^{-1}$ at 70°C [81].

Huang et al. [154] studied the mechanism of ion transport in PAN-based SPEs with different plasticizers. The ionic conductivity value obtained is of an order of 10^{-3} S/cm for all samples. The conductivity variation obeys the VTF behavior and activation energy obtained was 0.31 eV . At lower salt concentration conductivity increases is maximum at $N/\text{Li} = 8$ due to fast dissociation of salt at low concentration and at high concentration conductivity decreased again due to ion pair formation. The curvatures indicate that ionic conduction appears to obey the VTF relation, which describes transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase. Impedance analysis shows highest conductivity value is $6.72 \times 10^{-3} \text{ S cm}^{-1}$ for PVC (5)-PEMA (20)-PC (67)- LiBF_4 (8 wt.%) system and

is due to lower lattice energy (699 kJ/mol). Also, the curvature of Arrhenius plot follows the VTF relation [159]. Mohapatra et al. [166] studied the ion transport properties of PNC electrolyte based on PEO8- LiClO_4 dispersed with nanocrystalline of yttria stabilized zirconia (YSZ) using complex conductivity spectroscopy. A strong interaction of polymer matrix, mobile ions, and nanofillers results in faster ion dynamics along with improved dc conductivity on nanofiller dispersion. Janakiraman et al. [167] prepared electroactive separator based on PVdF- NaClO_4 + EC/DEC with DMSO as the solvent. The ionic transference number value is 98.30% and confirming the minimum concentration polarization. The ionic conductivity at 29°C is $7.38 \times 10^{-4} \text{ S cm}^{-1}$ that increased to $1.10 \times 10^{-3} \text{ S cm}^{-1}$ at 80°C . The activation energy of ion transport in the EASE is found to be 3.02 kJ mol^{-1} which is lower than the activation energies of PVDF copolymers in the literature.

Lee et al. [168] reported a composite electrolyte formation using PEO/PVdF + LiCO_4 and BaTiO_3 as nanofiller. The highest conductivity value was $1.2 \times 10^{-4} \text{ S cm}^{-1}$ for 15 wt.% filler concentration and at high content blocking effect dominates due to aggregation of fillers which reduces the ionic conductivity or mobility. Conductivity value increases

and highest is $7.13 \times 10^{-3} \text{ S cm}^{-1}$ by the addition of 15 wt.% nanofiller and may be due to the number of free ions and entrapment of solvent by ceramic phase increases the mobility. Another suggestion given was that ceramic particles may play the role as nucleation centers for the formation of the minute and provides a new path by polymer host and ceramic boundaries [152]. The addition of MMT to PVDF/PVA membrane could reduce the crystallinity of blending system, increase the proportion of amorphous phase, and thus promote the migration of lithium ions. The highest ionic conductivity up to $4.31 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature [82]. Nyquist plot shows the improved charge transfer process and absence of semicircle on the addition of nanofiller. For all filler doped samples conductivity is of the order of $10^{-4} \text{ S cm}^{-1}$ and is highest for BaTiO₃ nanofiller (i.e., $4.5 \times 10^{-4} \text{ S cm}^{-1}$) due to its high polarity and dielectric constant [169]. The conductivity variation shows maxima for 7.5 wt.% clay content with value $3.7 \times 10^{-3} \text{ S cm}^{-1}$ and increases to $7.8 \times 10^{-3} \text{ S cm}^{-1}$ at 100 °C for same clay content. As at high temperature migration of ions become fast, above glass transition temperature and direct coordination between ion and polymer host leads to greater flexibility with uniform transport. The double-layer capacitance (C_{dl}) value increases with temperature from 1.8 μF for pure PS to 15.6 μF for PNC and may be attributed to the accumulation of charge at an interface by the fast ionic transport [83]. The highest ionic conductivity was calculated using Cole-Cole plots and is $1.32 \times 10^{-3} \text{ S cm}^{-1}$ for 70 wt.% LiCF₃SO₃ content with PAN as polymer host [147].

The addition of clay increases the value of ac conductivity and at high clay content decreases and may be attributed to interaction of negative charges in the silicate layers with the Na⁺ cation of PS complex on immediate clay addition. At high clay concentration, viscosity of PNC increases and ion pair formation decreases the conductivity value. The highest electrical conductivity value is $\sim 2.20 \times 10^{-7} \text{ S cm}^{-1}$ for 5 wt.% clay concentration at room temperature. Variation of conductivity with temperature follows the VTF pattern [146]. Impedance plot shows an increase in dc conductivity from 1.01×10^{-5} to $1.20 \times 10^{-5} \text{ S cm}^{-1}$ after addition of nanofiller. Conductivity spectra shows an increase in conductivity with temperature and may be due to more ionic mobility which leads to the fast segmental motion of polymer and increase of ion concentration with temperature [170]. Arof et al. [171] prepared polymer electrolyte with PAN as polymer host and LiBOB as salt. The conductivity increases from $2.23 \times 10^{-10} \text{ S cm}^{-1}$ for pure PAN to $2.55 \times 10^{-5} \text{ S cm}^{-1}$ on the addition of salt. Lithium ion transference number was obtained in the range of 0.25 to 0.30. The double layer capacitance is high at low frequencies (35 F g⁻¹ at 10 mHz) and decreases with increasing frequency up to 100 kHz.

Pitawala et al. [172] reported the combined effect of plasticizer (EC) and nanofiller (Al₂O₃) on (PEO)₉-LiTf-based PE. It was concluded that with the increase of plasticizer (EC)

content there is an increase in the value of conductivity which was further incorporated by nanofiller. The highest value of conductivity was obtained for 50 wt.% EC and 15 wt.% Al₂O₃ with a value of $1.5 \times 10^{-4} \text{ S cm}^{-1}$. The highest conductivity obtained was $1.4 \times 10^{-4} \text{ S cm}^{-1}$ at 90 °C for the polymer-in-salt system with 80 wt.% LiPFAPB14 (M-80) and may be ascribed to the presence of excessive lithium cations and PFAPB14 anions disorders the polymer host domains due to the presence of formation of excessive lithium cations and PFAPB14 anions and leads to amorphous phase formation. The above enhancement in conductivity is also in agreement with the surface analysis done with SEM and 3D laser scanning confocal microscopy [173]. Poly(ethylene oxide) and poly(methyl methacrylate) blend-based SPEs consisting of lithium triflate as a dopant ionic salt with varying concentrations of PC as a plasticizer were prepared as reported by Sengwa et al. [174]. It concludes that the enhanced polymer chain segmental dynamics ordered ion–dipolar cooperativity and favorable ion conductive paths increase three times the ionic conductivity of 15 wt.% PC polymeric electrolyte film prepared by the ultrasonic-microwave-irradiated method as compared with that of the classical solution cast method.

Transference number analysis

In an ion-conducting solid conductor, both the ions (cations and anions) and electrons may take part in conduction process. Hence, it becomes essential to separate the current carried by which mobile species and referred as measurement of transport or transference number. There are two mostly used techniques:

(a) Ion transference number

This technique is used to separate the different contribution of electrons and ions from total charge transport. PE films are placed between two blocking electrodes SS|PEs|SS (stainless steel electrodes) and current is monitored as a function of time by applying the small dc voltage ($\sim 20 \text{ mV}$). The current decreases with increase in time due to polarization of mobile ions at working/blocking electrodes. Initially, both the ion and electronic part contributes but after some time current either approaches zero (for pure ion conductor) or attains a residual constant value (for mixed ionic/electronic conductor). Therefore, the ion transference number can be estimated using the Eq. 1:

$$t_{\text{ion}} = \left(1 - \frac{I_c}{I_t} \right) \quad (1)$$

Where I_t is total initial current or due to ions or as a combined result of ion and electron contribution while constant residual current (I_c) is due to electrons contribution only.

(b) Cation transference number

This technique has been proven to be applicable in circumstances where correction for passivating layer is required and particularly used for polymer electrolytes. Here, a small constant potential is applied by placing the PEs between two non-blocking lithium electrodes and the cation transference number is obtained by taking ratio of steady-state cationic current to the initial current just after switching-on the polarizing voltage. The additional contact resistance at electrodes due to passivating layers causes corresponding voltage drop which need to be subtracted from the applied potential difference. The contact resistance is determined by impedance measurements shortly before and after the potentiostatic polarization. The cell is being polarized by application of small dc voltage (~10 mV). The cation transport number is given by Eq. 2:

$$t_{\text{cation}} = \left(\frac{I_s(V - I_o R_o)}{I_o(V - I_s R_s)} \right) \quad (2)$$

Where, V is the applied dc voltage for sample polarization, I_o and I_s are the current before and after polarizations whereas R_o and R_s are the initial and steady-state resistance of the passivating layers [175].

Mohapatra et al. [153] reported the charge transfer to be predominantly ionic in nature with T_{ion} is 0.99 for 1–2 wt.% SnO_2 . Yang et al. [168] studied a sodium ion conducting gel polymer electrolyte based on PVdF-HFP and the transference number obtained is 0.995 and evidence of good ionic conductor. Sharma et al. [83] observed ionic transference number 99% based on polymer–salt $(\text{PAN})_8\text{-LiCF}_3\text{SO}_3$ complex into DMMT clay. Ma et al. [82] prepared a composite solid polymer electrolyte (CSPE) based on MMT nanoclay fillers, LiTFSI, PVdF, and PVA copolymer and lithium ion transference number of 0.40 was achieved. Stolarska et al. [176] studied the gel polymer electrolyte membranes composed of PVdF-HFP and surface-modified aluminum or titanium oxide, and lithium cation transference number of 0.66 was obtained.

The separation of ion and electronic contribution is done and the pattern of variation shows a very high initial total current (I_t) followed by a sharp drop in its value with the passage of time. Later, the current ultimately attains a saturation value and remains constant with time. The initial high current is attributed to the contribution from both the ions and the electron in the sample matrix whereas the final saturation current is attributed to the contribution of electronic mobility. It is known as residual electronic current (I_e). The transport number value is 0.99 and clearly indicates that the PNC samples are the predominantly ionic conductor. Polu et al. [75] investigated PVA as host polymer and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) as salt. A high value of ionic transference number (0.98) at 30 wt.% salt confirms that charge transport in

PS is dominated by ions and almost negligible contribution from the electrons (Fig. 19). The separate the cation and anion contribution from total transport number dc/ac impedance technique is used for 12 h. The estimated value of cationic transport number (t_{Li^+}) for PAN + LiCF_3SO_3 + 15 wt.% DMMT film is ~67%. It is higher in comparison with a number of polymer (PAN)–salt complex such as PAN- LiClO_4 (~60%), PAN- LiAsF_6 (~40%), and PAN- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (~60%). A comparison of the cation transport values suggests a clear enhancement in t_{Li^+} on intercalation of PAN + LiCF_3SO_3 complex into the nanometric clay galleries of the organo-modified clay [177]. Ghosh et al. [178] reported transference number for electrolyte films made from diblock copolymer PEO-*b*-PMMA-*ran*-PMAAL and the LiBOB salt, and value is 0.89 as shown in Fig. 20.

Ion transport mechanisms in PEs

The phenomena of ion transport in PEs is complex and depends on various factors such as cation size, dielectric constant of host polymer, ion pairing, amorphous phase character, and conduction by both the mobile ion types (cations and anions). A number of models such as, free volume theory, configurational entropy model, VTF behavior, WLF behavior, EMT approach, etc. have been proposed by different renowned scientific groups to interpret the ion conduction mechanisms in polymer electrolytes. A crucial role of theoretical developments in an area such as solid polymer electrolytes, which is growing rapidly and is based on quite complex materials, is to provide a set of models upon which interpretations of a given set of experimental data can be based. Two main mechanisms for the cation conduction in solid compound are the Grotthuss mechanism (proton hopping or

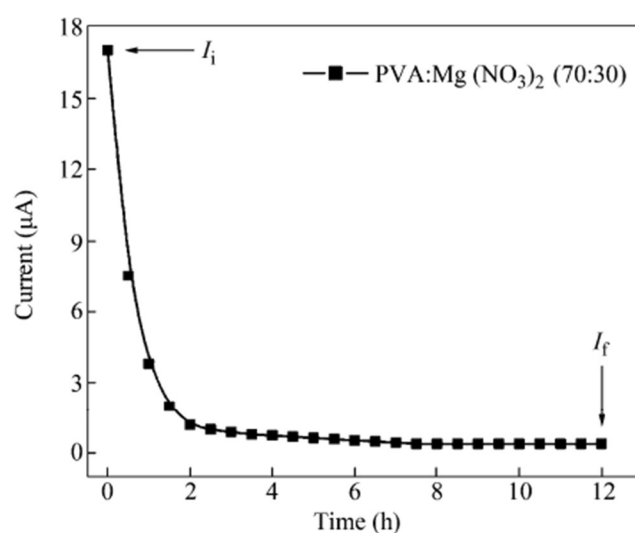
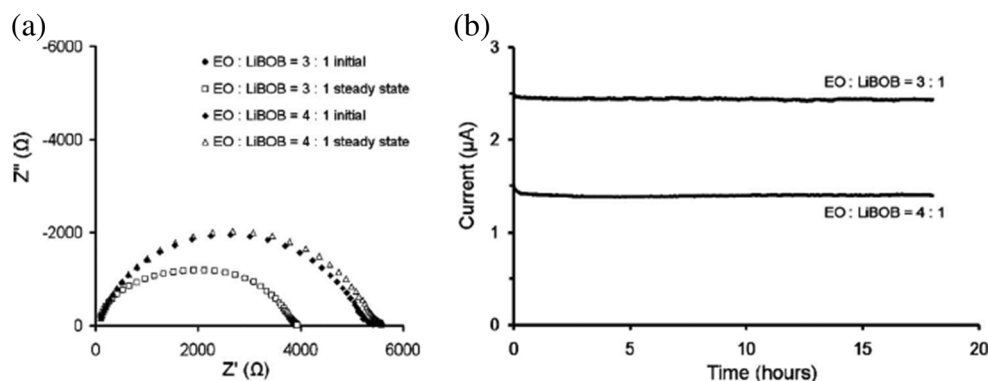


Fig. 19 Polarization current versus time plot of (PVA + $\text{Mg}(\text{NO}_3)_2$; 70:30) electrolyte film (reprinted with permission from [75], copyright Elsevier 2013)

Fig. 20 **a** Impedance scans from two electrolyte samples taken before and after potentiostatic measurements at room temperature 21–23 °C. **b** Current vs time profile of the polymer films, obtained at room temperature, under a 10-mV dc bias (with permission from [178], copyright ECS 2010)



structural diffusion) and the vehicle mechanism [181, 182]. The plastic crystal-doped ion diffusion involve coupling to certain, rotational, motions while in polymer electrolytes structural dynamic occurs due to whole polymer chain [181].

Armand et al. [182] for the first time explained the ion transport mechanism in PEO-alkali metal salt complexes (PEO-KSCN and PEO-NaSCN). The paper reports that the cation of the salt resides inside the single or double helices of polyether chains. In the classical PEO-salt complexes, transport of the cation was suggested to occur by hopping through the helices and the anions were assumed to be almost immobile and placed outside the helices (Fig. 21a). Molecular dynamic simulations suggest that the Li^+ ions are complexed to PEO through approximately five ether oxygens of a PEO chain, and that the mobility of the cations is decreased considerably by this complexation [183]. Consequently, the mobility of the Li cations is related to the motions of the complexing segments of the PEO chain. Thus, the cation transport is described as the motion of the Li^+ species between complexation sites assisted by the segmental motion of the PEO matrix (Fig. 21b). Later, Papke et al. [12] suggested that the transport of the cation, complexed within the helical regions, occurs through the disordered amorphous phase of the polymer electrolyte. In polymer electrolytes, lithium ions are coordinated by the electron donor group as in PEO (Fig. 21c). As a result of the motion of polymer chains, cations can move between coordination sites, either on one chain or between neighboring chains, called intrachain hopping and interchain hopping. Moreover, considering ion association from the ion–ion interactions between ions, there are other types of hopping mechanisms involving ion clusters as shown in Fig. 21c.

Free volume model

It is one of simplest transport mechanism used to understand the polymer ion transport and segmental mobility given by Cohen and Turnbull in 1959 [184]. It is based on assumption that motion in a polymer electrolyte depends on the redistribution of free volume associated with

the end of a polymer chain in the matrix not on thermally activated process. The increase in temperature expands

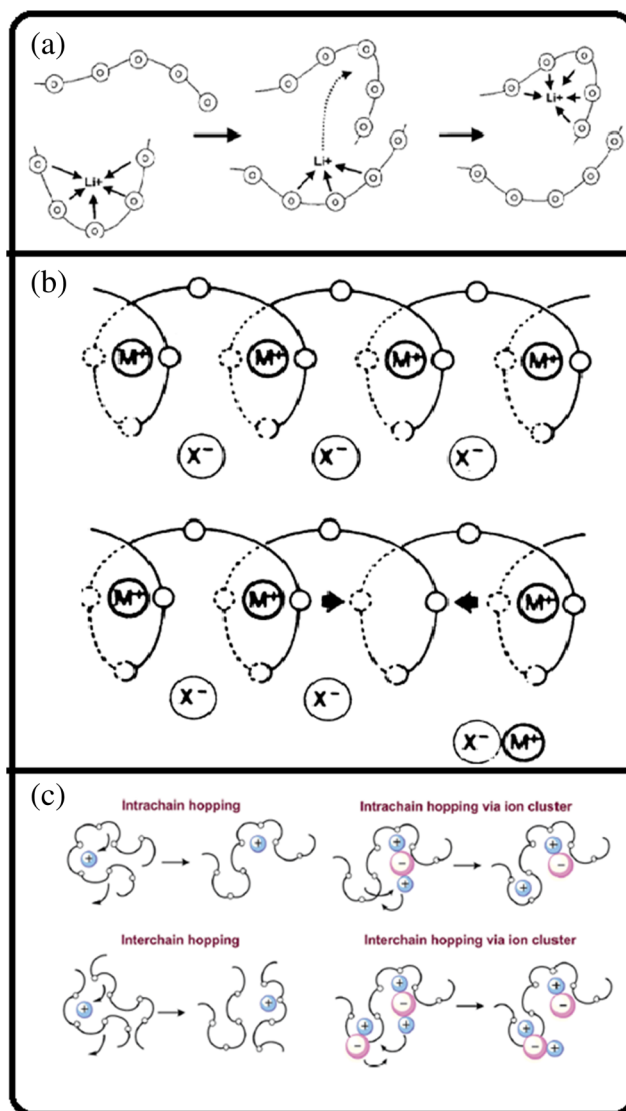


Fig. 21 **a** Schematic of the segmental motion assisted diffusion of Li^+ in the PEO matrix. The circles represent the ether oxygen of PEO (printed from ref. [4]). **b** A reproduction of the first page of *Polymeric solid electrolytes* by Armand, Chabagno, and Duclot, taken from the extended abstract, (printed from ref. [3]). **c** Mechanism of ion transport in PEO (reprinted with permission from [12], copyright ECS 1982)

the material and creation of voids leads to free volume enhancement which provides more free space to polymer segmental motion. This increase in free volume increases the ability of polymer chain to rotate freely which directly affects the ion transport and obeys the following relation expressed by Eq. 3:

$$V_f = V_g(0.025 + \alpha(T - T_g)) \quad (3)$$

Where V_g is the critical volume per mole at T_g , α is the thermal expansivity, and T represents the temperature during experiment. The biggest drawback faced by this model are that it ignores the kinetic effects associated with long chain molecule and does not involve the microscopic behavior like dielectric relaxation, effect of the molecular weight in transport properties, etc.

Configurational entropy model

Gibbs et al. [185] proposed this model to overcome the drawbacks of free volume model. One fundamental difference between free volume model and entropy model is that the former is based on volume while the later on the entropy concept [185]. As entropy model is based on the cooperative rearrangement of the polymer chains while free volume model includes transport via the formation of voids. The average probability of chain arrangement is given by the Eq. 4;

$$W = A \exp\left(-\frac{\Delta\mu S_c^*}{k_B T S_c}\right) \quad (4)$$

Where, A is pre-exponential constant, k_B is the Boltzmann's constant, T is absolute temperature (K), S_c^* is minimum configurational entropy required for the rearrangement, S_c is configurational entropy at temperature T , and $\Delta\mu$ is apparent activation energy opposing the rearrangement of polymer segmental unit (kJ/mol).

Vogel–Tamman–Fulcher model

The Vogel–Tamman–Fulcher model can be explained by free volume theory and was developed by Vogel, Tamman, and Fulcher in the early part of the twentieth century, for diffusion in the glassy system or viscosity of supercooled liquids. According to this theory, the ionic transport mechanism in the polymer electrolyte results from the segmental motion. This process promotes ion movement through the formation and destruction of a co-ordinating sphere of the solvated ion, thereby, creating a free volume into which the ion could diffuse under the

influence of the electric field VTF equation derived using entropy model can be expressed by Eq. 5:

$$\sigma = \frac{A}{\sqrt{T}} \exp\left(-\frac{B}{T - T_0}\right) \quad (5)$$

Where, A is a constant proportional to the number of carrier ions, B is the pseudo-activation energy of the ion, and T_0 is the equilibrium glass transition temperature or pseudo-transition temperature ($<T_g$).

As it is well known that ion transportation occurs above the T_0 , which is due to relaxation and transport processes as suggested by VTF model [188, 189]. This model is based on assumption that the transport in polymer electrolytes occurs in the amorphous phase content of the host polymer. As above the glass transition temperature, disorder takes place in polymer chains which changes the entropy and promotes the ion transport. The application of this model is limited to the single-phase amorphous systems and cannot be generalized. Luo et al. [190] reported that phosphonium-based protic ionic liquids (PILs) exhibit higher thermal stability and ionic conductivity than the corresponding ammonium-based PILs, no matter whether the P and N center atoms are bonded to the electron-donating octyl groups or the electron-withdrawing phenyl groups. The ion conduction behavior of the PILs can be adequately described by the VTF equation, and higher ionic conductivity of phosphonium-based PILs may be attributed to their weaker hydrogen bond and Coulombic interactions as well as higher carrier ion concentrations, indicated by infrared analysis, lattice potential energy estimation, and VTF fitting results as in Fig. 22 (I (a,b)). Another study concluded that the ionic conductivity of the whole system followed the prediction of the VTF equation very well as in Fig. 22 (II (a,b)) [189].

Later, Williams, Landel, and Ferry [190] developed extension of VTF equation named as WLF equation, to study the dynamics of polymers and other glass forming materials. In this equation, they considered not only the effect of viscosity but also the inherent relaxation processes which characterize any glass forming materials. This modified version of the VTF model can be explained by Eq. 6;

$$\log a_T = \left(\frac{\{-C(T - T_s)\}}{(C_2 + T - T_s)} \right) \quad (6)$$

Where, a_T is shift factor and is ratio of mechanical relaxation process at ordinary temperature T to some reference temperature T_s .

The temperature dependence of conductivity which obeys the VTF equation confirms the free volume ion transport mechanism in polymer electrolytes and concludes that the micro-Brownian motion of polymer chain

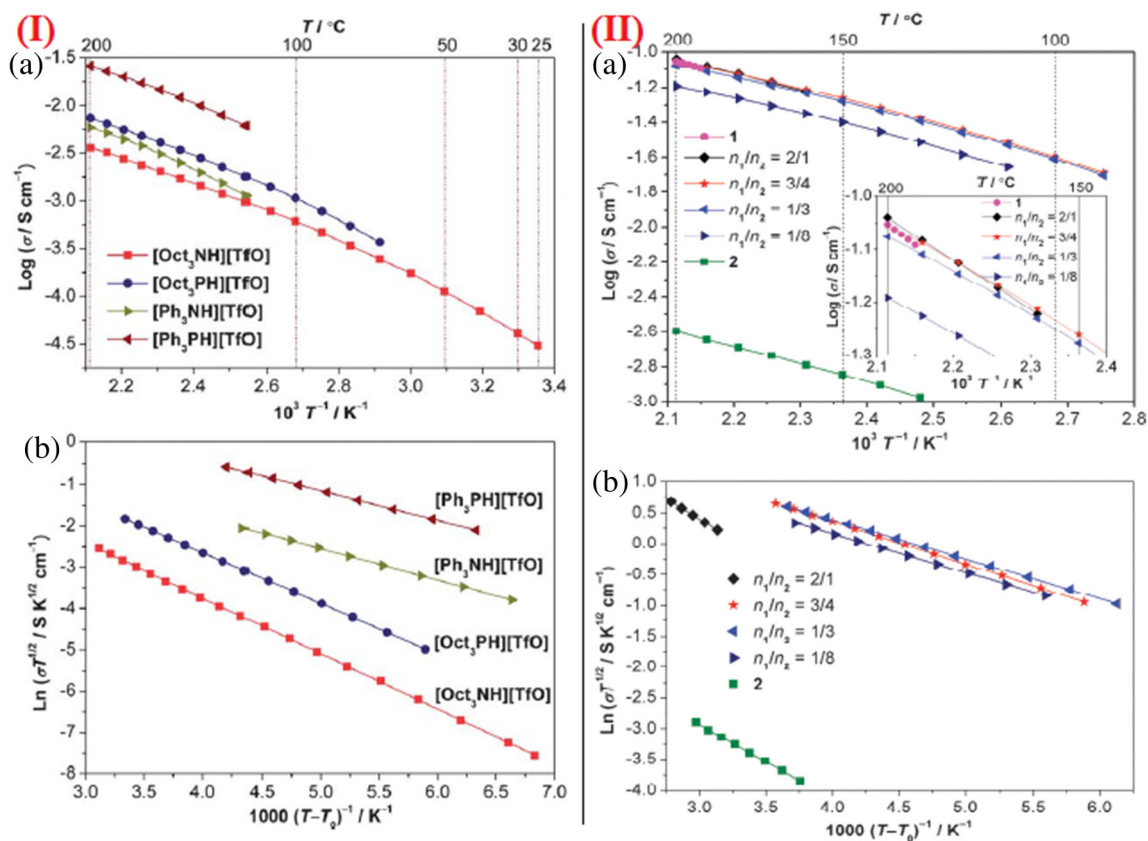


Fig. 22 I Arrhenius plots (a) and VFT plots (b) for the ionic conductivity of phosphonium-based and ammonium-based protic ionic liquids (reprinted with permission from [190], copyright RSC 2012). II

segment affects the ionic transport which supports the transport in amorphous phase. Further, investigation were done using WLF theory to clarify the ionic conductivity mechanism by using relationship between ionic conductivity and fractional free volume $f_r(T)$ [191]. It concludes that ionic conductivity increases with increase in fractional free volume as shown by linear relationship in Fig. 23 and can be described by the following equations (Eqs. 7 and 8):

$$f_r(T) = f_r(T_g) + \alpha(T - T_g) \quad (7)$$

$$\log_{10}\sigma(T) = \log_{10}\sigma(T_g) + C_1 \left(1 - \frac{f_r(T_g)}{f_r(T)} \right) \quad (8)$$

Angels decoupling theory

Ion transport mechanism in polymer electrolytes was later enlightened by Angell [192] based on assumption that coupling between transport and relaxation plays an active role in ion transport. As it is well known that polymer segmental motion occurs above the T_g , the VTF model can be generalized as said above, so Angell generalized the ion transport

Arrhenius plots (a) and VFT plots (b) for the ionic conductivity of the $C_3H_5N_2^+-CH_3SO_3-C_2H_5N_3$ system. For VFT plots, the lines represent the VFT fittings (reprinted with permission from [188], copyright RSC 2012)

mechanism using a new term decoupling index (R_τ) denoted by Eq. 9:

$$\text{Decoupling index } (R_\tau) = \frac{\text{Structural relaxation time } (\tau_s)}{\text{Electrical relaxation time } (\tau_\sigma)} \quad (9)$$

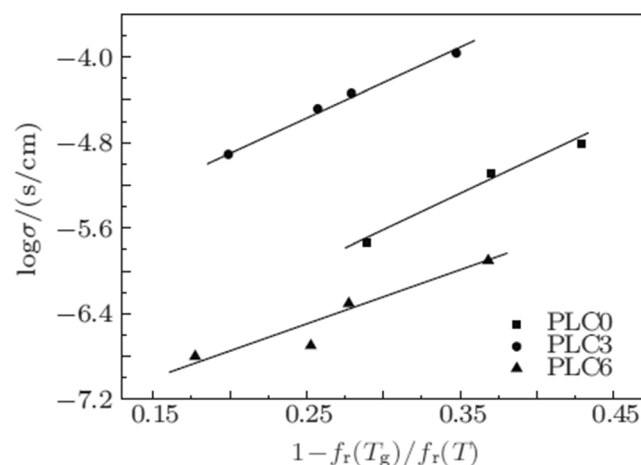


Fig. 23 Variations of $\log\sigma$ with $1 - f_r(T_g)/f_r(T)$ for PEO-LiClO₄-clay composites (reprinted with permission from [191], copyright Institute of Physics 2012)

Here, τ_s refers to the segmental relaxation or viscosity and (τ_σ) is inversely proportional to the conductivity. A larger value of R_τ reflects highly decoupled charge conducting modes by the viscous motion of the matrix. If $R_\tau = 1$, then the ionic motion and the structural relaxation occur at the same time and for polymer–salt complexes $R_\tau < 1$, which indicates rapid structural relaxation than the conductivity relaxation. The relaxation process, which allows the rearrangement of the polymer structure, may or may not help in ion dynamics and may be attributed to the inter-ionic interaction, which results into ion immobilization [193]. Dam et al. [86] in 2015 reported a solid polymer electrolyte and correlated the segmental and conductivity relaxation time using decoupling index. Figure 24 shows the variation of R_τ as a function of temperature for various compositions. And it is observed that R_τ is having values in the range of 5 to 48 which suggests that ion conduction is very closely coupled to the segmental relaxation.

Amorphous phase model

Various reports on the study of polymer electrolytes suggest that addition of nanofiller decreases the crystallinity and amorphous phase content increase which leads to faster ion transport. This is the assumption for the amorphous phase model [194]. Within the polymer host, ionic transport is sustained by polymer segmental motion and is thus faster within the amorphous region than within the crystalline region of the polymer host. For example, in the crystalline PEO-salt complex systems, the filler particles (e.g., α - Al_2O_3) act as nucleation centers in the crystalline PEO-salt complex systems and possibly

attach to PEO segments through acid Al surface centers. Presence of large numbers of nucleation centers in the polymer electrolytes promotes crystallization process and, as a consequence, bigger disorder, typical of a liquid state, is frozen in the newly formed solid polymeric matrix on solvent evaporation. However, this requires more observation, especially in terms of the absolute crystallinity measurements rather than a relative value of the system.

Effective medium theory

Effective medium theory was originally developed by Nan and Smith in 1991 [195] for polymer electrolytes based on simple effective medium equation of Landauer in 1952 [196]. It can be applied to explain the electrical properties in composite polymer electrolytes, composite solid electrolytes, etc. [197]. The improvement in the conductivity is obtained with addition of nanofiller and may be due to the change in microstructure at electrolyte-filler interface. According to the theory, there are three components present in a composite polymer electrolyte with different electrical properties, (i) the highly conductive interface layers coating on the surface of the grain, (ii) the dispersed insulating fillers in polymer host matrix, and (iii) the dispersed filler throughout the polymer electrolyte host matrix and the highly conducting interface layer makes a matrix phase which is consist of overlapping/touching units providing high conducting pathways in polymer matrix.

According to the Maxwell Garnett rule [198], the equivalent conductivity (σ_c) of the CPEs unit can be expressed by Eq. 10:

$$\sigma_c = \frac{2\sigma_1 + \sigma_2 + 2Y(\sigma_2 - \sigma_1)}{2\sigma_1 + \sigma_2 - Y(\sigma_2 - \sigma_1)} \quad (10)$$

Here σ_1 and σ_2 are, respectively, the conductivity of interface layer and that of dispersed insulating grain. Y is the volume fraction of dispersed grain in a composite unit and for spherical geometry which can be calculated by Eq. 11:

$$Y = \frac{1}{\left(1 + \frac{t}{R}\right)^3} \quad (11)$$

Where, t is the thickness of interface layer and R the radius of dispersed grain. t/R parameter is based on assumption that an increase in amorphous phase content in CPEs in comparison with pristine system is due to amorphous present in the surface [199].

In the CPEs, enhancement in the conductivity or mobility strongly depends on the grain size distribution, and the composite grain size. Smaller volume fraction of the insulating phase promotes the conductivity of the composite electrolyte to the maximum. The above model was further improved by

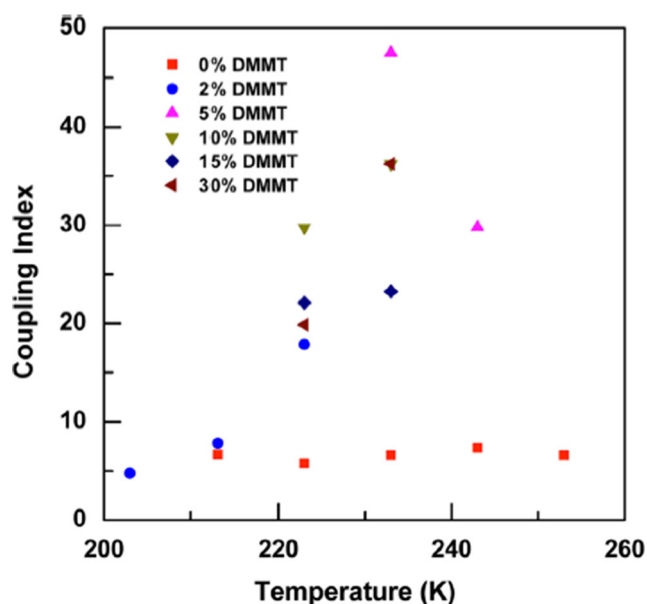


Fig. 24 Decoupling ratio as a function of temperature for different DMMT concentration (reprinted with permission from [86], copyright Springer 2015)

Wieczorek et al. [194] who report that the interface layers are structurally amorphous and its glass transition temperature-dependent conductivity follows VTF equation. The three phases in a CPEs are schematically shown in Fig. 25, which contains a highly conductive layer covering the surface of the grain (phase 1), dispersed filler grain (phase 2), and the bulk polymeric electrolyte (phase 3). The formation of a high conductive pathway composed of the surface layers, i.e., phase 1, is proposed to be the possible region of enhanced conductivity of the composite polymer electrolyte.

Transport mechanism in dispersed polymer electrolyte

Ionic conductivity of the composite polymer electrolytes depend on the equilibrium of the Lewis acid–base interactions. The nature of interaction is dipole–dipole interaction, and polymer phase acts as an ion transport medium. The Lewis acid group of nanofiller may compete with Lewis acid lithium cation for the formation of complex with polymer host. The hydrogen bonding present between host polymer and nanofiller promotes the fast ion transport by perturbing the chain and increases the free space volume. The Lewis acid groups of the added ceramics may quite likely compete with the Lewis acid lithium cations for the formation of complexes with the polymer chains, as well as with the anions of the added alkali salt. The ceramic surface group may act as crosslinking centers for the host polymer and anion, which lowers the structure reorganization tendency and promotes faster ion transport. Also, filler surface group acts as Lewis acid–base interaction centers with the polymer/salt and ionic decoupling promoting more salt dissociation which directly enhances the free number of charge carriers and hence conductivity [200]. Lewis acid–base coordination between the hydroxyl group attached on Y_2O_3 surface and the oxygen of

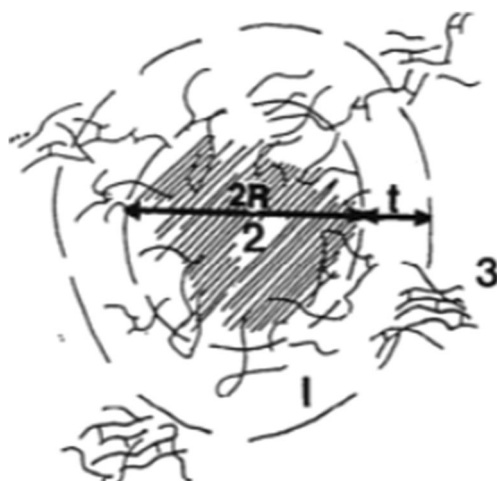


Fig. 25 Schematic representation of composite electrolyte. Symbols are the same as in the text (reprinted with permission from [194], copyright Elsevier 1989)

the ether of PEO comprises the major interaction as reported by Liang as in Fig. 26 [201]

Transport mechanism in intercalated polymer electrolyte

In an intercalated type of polymer electrolytes, polymer structures occupy the gallery of clay due to an interaction between clay surface and polymer electron donor group due to the creation of surface charge (Fig. 27). Figure 27a shows that the complexes of PEO molecules confined within PMMA domain enter between the MMT platelets and increased the clay gallery spacings [202]. The adsorption of polymers on the MMT surfaces also exfoliates the MMT nanoplatelets and forms the exfoliated nanocomposites. The Li^+ has four to six sites of coordination with the electron-donating groups of polymers and also the negatively charged MMT nanoplatelets. The various interaction between polymer/salt/filler like $EO-Li^+$, $C=O-Li^+$, $MMT-Li^+$, and $C=O-Li^+-EO$ makes nanocomposites and anion remain uncoordinated somewhere in the polymer backbone (Fig. 27b).

Tang et al. [203] in 2012 reported that nanotubes could be packaged within insulating clay layers to form effective 3D nanofillers. The growth of CNTs within clay interlayers leads to partial exfoliation of clay platelets and the formation of a hybrid filler with a high aspect ratio which leads to the interaction between clay, carbon nanotubes, polymer chains, and a lithium salt as shown in Fig. 27c. The lithium cation interacts with both the high negative charge of the electron cloud in the outer surface of CNTs as well as the negative oxygen atoms on the clay. This dual interaction mechanism leads to separation of the contact-ion pairs. Also, the unfolded polymer chain enhances the free volume due to the high aspect ratio of the 3D hybrid nanoscale fillers packaged with CNT. Increase in free volume directly suggests the higher mobility of ions due to least resistance paths in the polymer.

Shukla et al. [204] in 2010 reported the possibility of exfoliation at lower clay loading and intercalation with an increase in clay concentration in the composite matrix and proposed a mechanism for transport of ions. Out of two possible

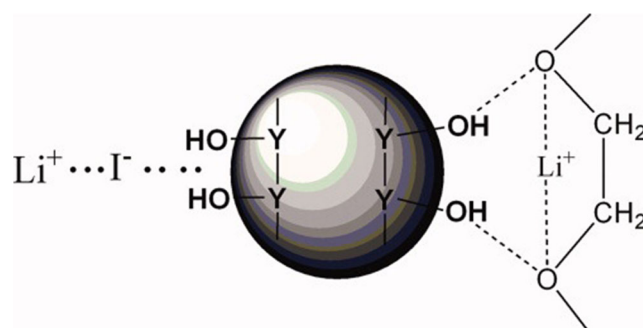


Fig. 26 The pictorial model of the surface interactions between the Y_2O_3 nanofiller and the PEO-LiI matrix in the SPEs (reprinted with permission from [201], copyright Wiley 2011)

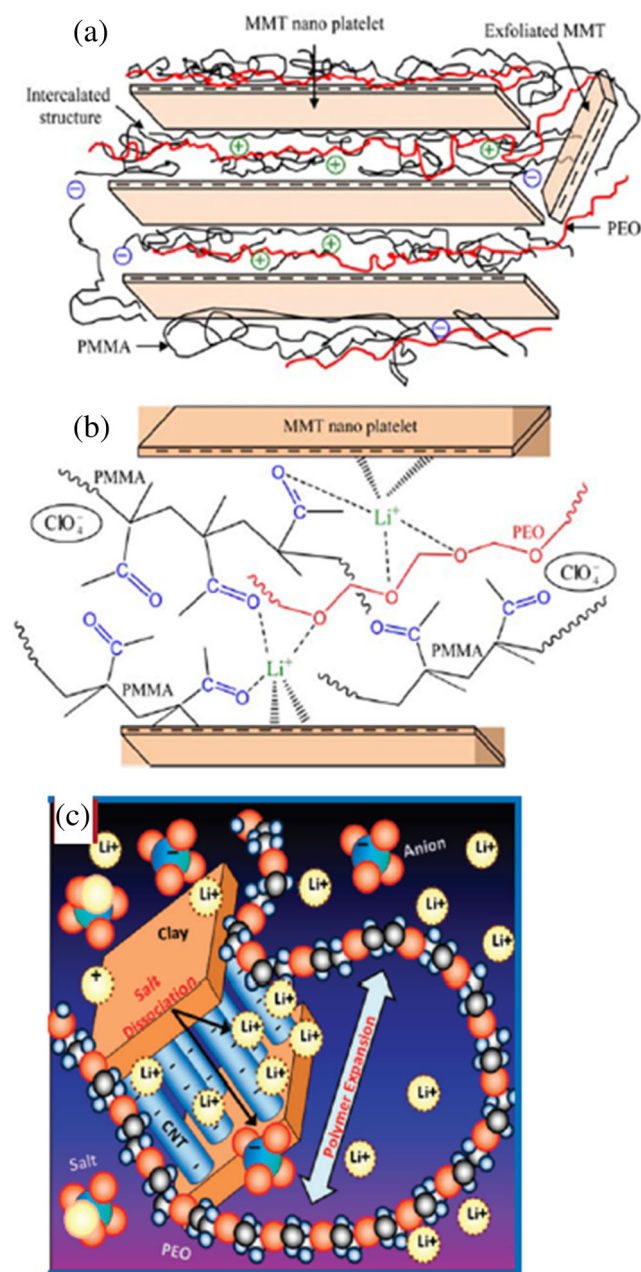


Fig. 27 Schematic representation of **a** intercalated and exfoliated MMT structures, **b** ion–dipolar and ion–ion interactions in cation-coordinated polymer-blend-intercalated MMT structure in the (PMMA-PEO)-LiClO₄ - *x* (wt.%) MMT nanocomposite electrolyte film (reprinted with permission from [202], copyright Wiley 2015), and **c** schematics of the interactions between clay, carbon nanotubes, polymer chains, and lithium salt ions (reprinted with permission from [203], copyright ACS 2012)

interaction sites ($C=O$ and $O-CH_3$) for coordinating the cation in the backbone of PMMA, the lithium cation coordinates with the $C=O$ site of the PMMA due to its stronger electron donicity than $O-CH_3$ as shown in Fig. 28a (i). This polymer ion interaction is of two types; (a) direct coordination of cation with $C=O$ of the polymer chain as depicted in Fig. 28b (i) and (b) cation (Li^+) coordination with the $C=O$ group of polymer

chain bridged by anion. Figure 28c shows that cation-coordinated polymer chains are inside the nanometric channels provided by clay and is supported by both Coulombic interactions as well as the thermodynamics. The silicate layers of the clay play the role of Lewis base due to the negative charge on surface and helps in dissociation of the salt by breaking coordinate bond with the polymer backbone via clay–ion interaction [205]. At low clay content when the PS matrix enters the clay galleries, the clay exfoliated occurs due to the interaction between negative charges in the silicate layer with the lithium cation (Fig. 28d). This interaction reduces the ion pairing effect as shown in Fig. 28e (i). The ion–clay interaction results an increase in the fraction of free ions and ion cluster formation occurs at high clay content (Fig. 28d, e (i–iii)). At high clay concentration intercalation of clay restricts the movement of bulky anion due to coulombic interaction and allows only the lithium cation motion in the clay gallery. The negative charge on silicate layer weakens the polymer cation interaction and results in an increase in the fraction of free ion (Fig. 28f (ii)). At high clay loading, the free mobile charge carriers get trapped due to the random distribution of clay particulates in the composite phase (Fig. 28e (iii)) and decreases both mobility and conductivity.

In the same line a model was proposed by Sharma et al. [206] to explain the filler/clay-dependent changes in electrical properties of the composite phase. Report says that in pristine PS matrix, Li^+ cation may get coordinated at the most with four, five, or six electron-rich nitrogen ($-C\equiv N$) sites of the polymer host matrix due to polymer–ion–clay interaction and the bulky anion (PF_6^-) is leftovers hanged somewhere in the host polymer backbone (PAN) as an uncoordinated free anion as in stage 1 of Fig. 29. There are two possibilities of coordination, one is direct coordination of cations with electron-rich site host polymer and another is coordination of cations to polymer chain bridged by anions and former one is viable during the PS complexation. The presence of negative charge at clay surface galleries interact with cation by coulombic interaction which favors polymer chains access into clay galleries and is thermodynamically feasible ($\Delta G = -ve$) as shown in stage 2 of Fig. 29. The coulombic interaction between the number of channels available in the clay and quantity of cation coordinated polymer chains generates an imbalance resulting into the rupture of clay platelets. This rupture in clay platelets result into clay exfoliation (stage 2 (2A)) at lower concentration and clay intercalation (stage 2 (2B)) at high clay content. The clay intercalation at high content may be attributed to increase in number of available clay galleries that enhances the possibility to accommodate larger fraction of cation coordinated stage 3 suggests that there is possibility of polymer–clay and ion–clay interaction which enhances the fraction of free anions [207]. The net conductivity enhancement, at low clay loading is due to direct interaction of clay platelets with the Li^+ coordinated polymer and at high clay content,

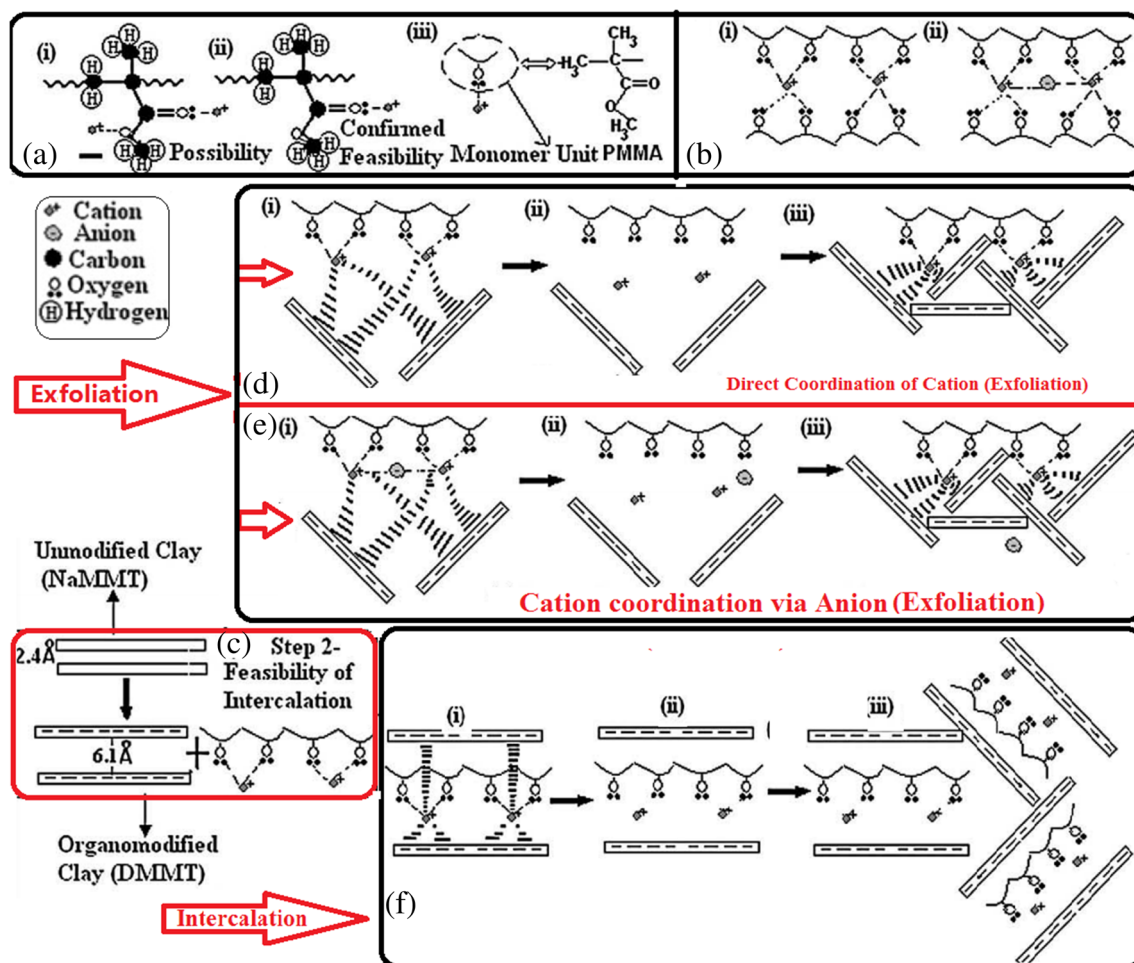


Fig. 28 Scheme showing clay-ion interaction and proposed mechanism for ion transport in the PNC films (reprinted with permission from [204], copyright Elsevier 2010)

redistribution leads to exfoliated to intercalated nanocomposite structure (stage 3). The conductivity drop at elevated clay concentration may be related to the random/disordered distribution of clay particulates in the composite phase (Fig. 29 (stage 3C)).

Stability analysis

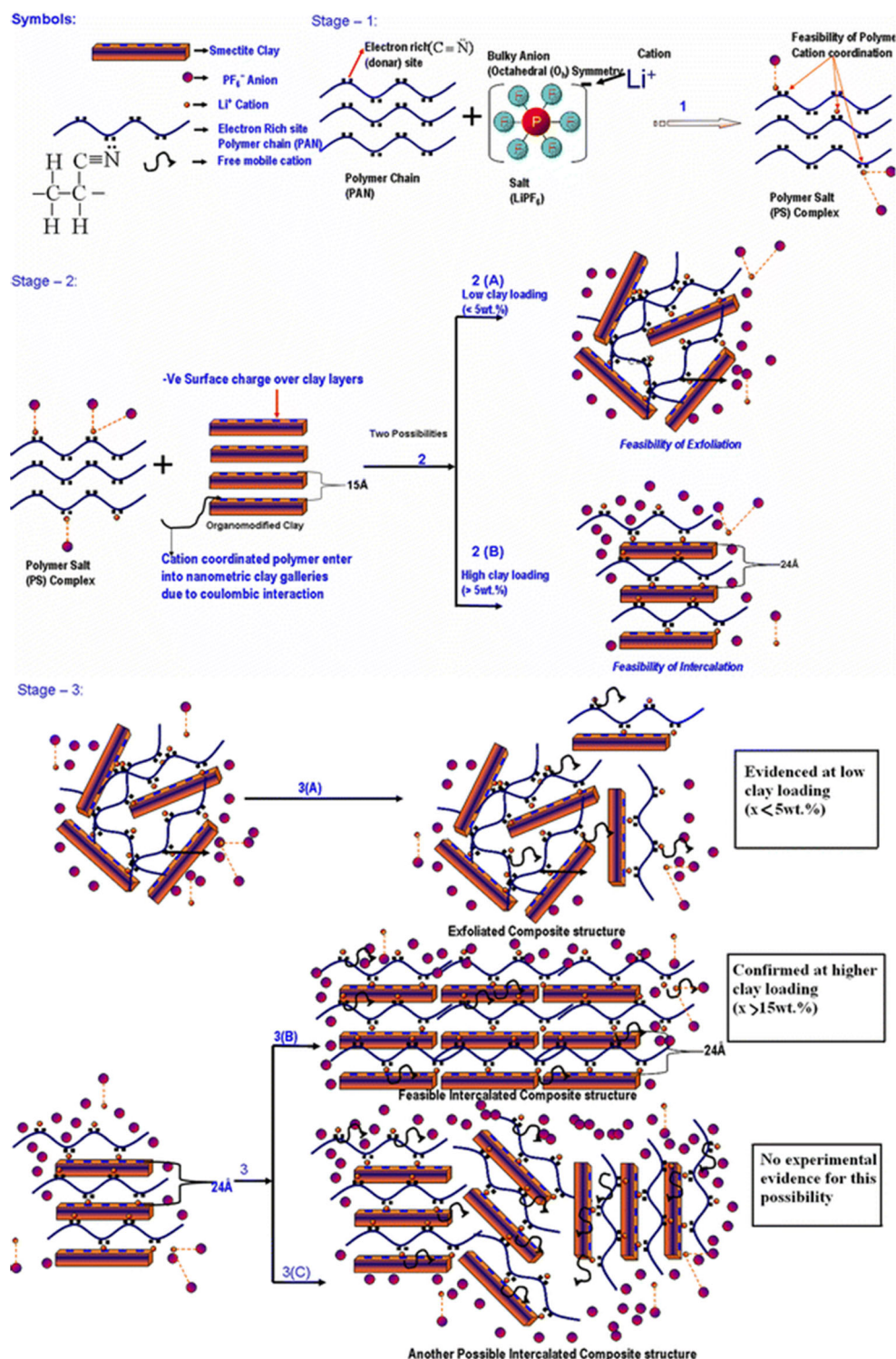
Thermal stability

In thermal stability, analysis are mainly focused towards phase transition, heat of reaction, oxidative stability, and various thermos-dynamical process occurring in the sample. The ion conduction property of solid ionic conductors depends on the thermal stability of the material. The glass transition temperature in the solid ionic conductors affects the ion conduction and crystal structure. Thermogravimetric analysis (TGA) is the basic technique to study the degradation temperature and other parameters of solid. Here, sample is held at constant temperature and change in mass of the sample is recorded to study the

chemical nature and stability of the material. Differential scanning calorimetry (DSC) is an important technique to study the phase transitions, thermal stability and glass transition temperature of the sample. A sample with an inert reference sample is placed at the same temperature and heated separately to plot the heat input as a function of temperature and time. The physical/chemical changes of the sample are visible by endothermic peak appearing due to absorption of heat. Also, exothermic peak is seen corresponding to the exclusion of energy suggesting changes in the material.

Li et al. [208] reported the preparation of nanofibrous membranes based on PVdF doped with ion complex (SiO_2 -PAALi) by electrospinning technique. TGA analysis shows thermal stability ranging up to 450 °C and may be due to the presence of interaction between host polymer and ion complex. Liang et al. [81] investigated the PEO-PMMA-based SPE with LiClO_4 and LiTFSI as salt and nano- Al_2O_3 as nanofiller. TGA study (Fig. 30) shows that mass attenuation is less for nanofiller-doped PS complex (6.1%) than PS complex (7.3%), and this decrease

Fig. 29 Scheme based on ion conduction mechanism, step 1: cation coordination with polymer backbone side, step 2: possibility of interaction of cation coordinated polymer with clay tactoids, and step 3: release of free charge carriers (cations) from the coordinated polymer chains on addition of clay in the PNC films (reprinted with permission from [206], copyright Springer 2011)



proves that nanofiller improves the thermal stability and can be used for the battery system. Also, thermal stability is higher for polymer host blended with LiTFSI than LiClO_4 . TGA curve shows an excellent thermal stability with LiBF_4 , LiClO_4 and LiCF_3SO_3 as salt with PVC/PEMA blend polymer and can be used up to 254 °C, 231 °C and 248 °C, respectively [168].

Lee et al. [168] reported a composite electrolyte formation using PEO/PVdF + LiClO_4 and BaTiO_3 as nanofiller. DSC curve shows the effect of nanofiller on melting and crystalline behavior of PS complex (Fig. 31). The T_m goes from 68.68 °C (Pure PEO) to 54.67 °C (20 wt.% nanofiller) and the crystallization temperature (T_c) was around 28–35 °C (Fig. 31b). Decrease in crystallinity

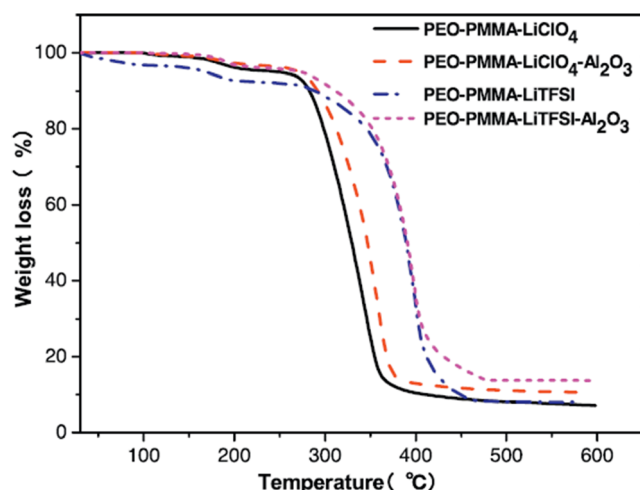


Fig. 30 TG curves of the polymer membranes from 25 to 600 °C under nitrogen flow (with permission from [81], copyright Elsevier 2015)

from 32.17% (0 wt.% nanofiller) to 22.69 on the addition of filler (20 wt.%) confirms the enhancement in conductivity. PVDF/PVA membrane is inferior to the PVDF/PVA/MMT composite membrane concerning thermal stability, as the initial decomposition temperature of the two samples is 150 and 180 °C, respectively [82]. TGA analysis [83] shows a broad stability range of the order of 200 °C for PAN-LiPF₆-DMMT and makes it suitable as an electrolyte with improved electrochemical, mechanical and thermal properties. DSC analysis for PEO/NaPF₆ system shows the lower melting temperature than other systems and may be due to different morphology, environment and molecular weight of host polymer [148].

Pandey et al. [209] studied a GPEs based on LiPF₆/IL/PVdF-HFP for supercapacitor application. TGA curve shows a thermal stability range up to 325 °C and suitable as a separator cum electrolyte for application in the electrochemical devices. DSC study shows an endothermic peak at 135 °C corresponding to the melting of the host

polymer. Further blending with ILsEMImFAP lowers the melting point substantially to 115 °C and is more asymmetric with less area. It may be due to the presence of liquid components in the larger proportion which improves the amorphous content. Pitawala et al. [172] reported the combined effect of plasticizer (EC) and nanofiller (Al₂O₃) on (PEO)₉-LiTf-based PE. DSC analysis shows the decrease in the value of glass transition temperature up to 560 oC and evidencing the polymer flexibility or greater mobility. Leo et al. [158] prepared composite polymer electrolyte based on PEO + lithium triflate (LiCF₃SO₃) with Li Nasicomound (Li_{1.4}(Al_{0.4}Ge_{1.6})(PO₄)₃) as the ceramic filler and EC + PC as the plasticizer. DSC study concludes the decrease in glass transition temperature with an addition of filler suggesting the softening of polymer chains and enhancement in polymer segmental motion.

Mechanical stability

It is one of the important parameter as it helps to optimize the suitability of material for application purposes. Different mechanical characterizations are available to study the mechanical properties as follows: In this technique, mechanical properties are varied w.r.t variation in stress and strain as a function of time. This method helps us to calcite the storage modulus, loss modulus, and dissipation factor. Ramesh et al. [210] investigated mechanical properties of a blend based on PVC-PEO as a host polymer, lithium triflate (LiCF₃SO₃) as a salt, mixture of EC and dibutyl phthalate (DBP) as plasticizers and silica (SiO₂) as the nanocomposite filler. The blending of PVC with PEO increases the Young's modulus value from 0.69 MPa (in pure PEO) to 5.13 MPa (in PVC-PEO = 70:30) and harder and more brittle blend is obtained due to the difference in the crosslinking density provided by PVC. Also, the addition of low molecular weight

Fig. 31 **a** DSC heating curves of **a** pure PEO, CPEs containing **b** no filler, **c** 5 wt.%, **d** 10 wt.%, **e** 15 wt.%, and **f** 20 wt.% of nanosized BaTiO₃. **b** DSC cooling curves for **a** pure PEO, CPEs containing **b** no filler, **c** 5 wt.%, **d** 10 wt.%, **e** 15 wt.%, and **f** 20 wt.% of nanosized BaTiO₃ (reprinted with permission from [168], copyright Elsevier 2013)

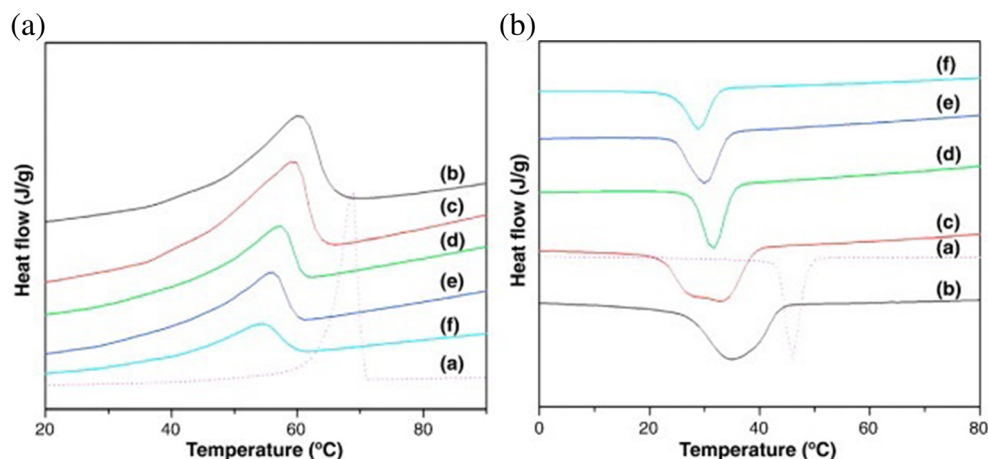
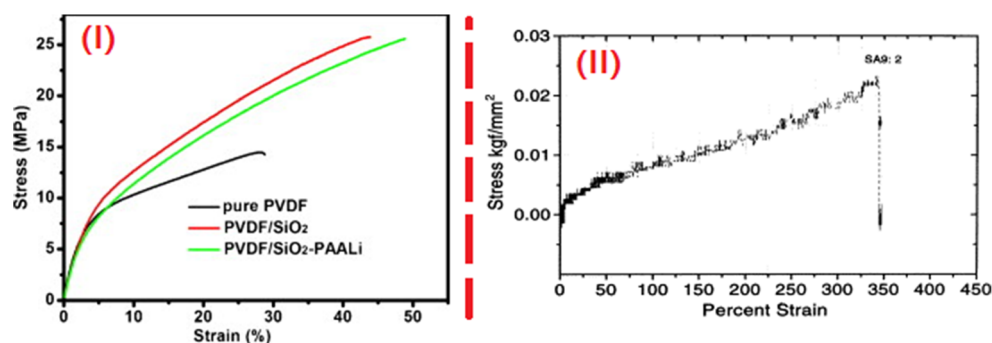


Fig. 32 I Stress-strain curves of the nanofibrous membranes (reprinted with permission from [208], copyright Elsevier). II Stress-strain curve for PVC-PEO-LiCF₃SO₃-DBP system (reprinted with permission from [210], copyright Elsevier 2007)



plasticizers to PVC-PEO-LiCF₃SO₃ decreases the modulus and stress at the peak of the complexes (Fig. 32 (II)). When the plasticizer content is increased (in binary plasticizer systems), there is an apparent decrease in modulus and stress at peak for the electrolytes. The elongation at peak values shows that the increase in plasticizer content reduces the elasticity of PVC-PEO-LiCF₃SO₃ complex.

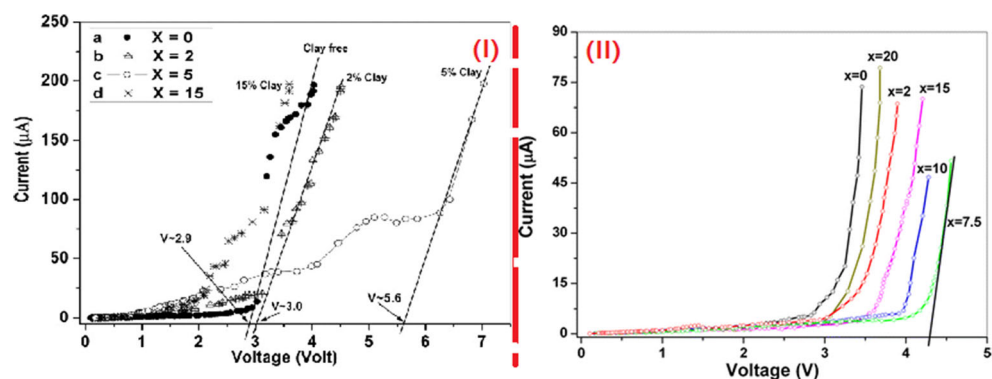
Kim and Oh et al. [211] also reported sane results on the blend of PMMA-poly(ethylene glycol dimethacrylate) (PEGDMA) complexes. The addition of salt in polymer blend decreased the Young's modulus and stress at peak values and attributed to the intramolecular mode of interaction of the Li⁺ with the polymer matrix. It also confirms the enhancement of amorphous phase on the addition of salt. After dispersing the nanofiller into the polymer blend mechanical properties are improved due to the presence of fillers at the interface between the phases [212]. The addition of plasticizers (DBP and EC) further decreases the Young's modulus value and improved the polymer flexibility. It was concluded that mechanical properties of polymer films is improved with the addition of nanosized silica. Stress and strain curve of PVdF/SiO₂-PAALi nanofibrous membranes shows stress value 48.8 MPa and strain value 25.6% (Fig. 33 (I)). Doping of nanoparticle improves the mechanical properties due to the large contact area between the dopants and PVdF nanofiber as an external force during under attack is absorbed firstly by the doped nanoparticle and occurrence of crazing effect enhances the mechanical properties [208]. The PEO-PMMA-LiTFSI-Al₂O₃ composite film shows higher tensile strength (3.26 MPa) as compared

with polymer-salt complex (2.78 MPa) and is greater for LiTFSI-doped composite than LiClO₄ (2.84 MPa). High tensile strength confirms the good mechanical properties of SPE [81]. Yang et al. [50] studied a sodium ion conducting gel polymer electrolyte based on PVdF-HFP. The mechanical analysis gives us satisfactory value of tensile strength and breakage elongation of the porous P(VdF-HFP) membrane 7.6 MPa and 148%, respectively. Leo et al. [213] reported the lithium ion conducting CPE based on (PEO)₈-LiCF₃SO₃ dispersed with a glass-ceramic and maximum tensile strength obtained was 22.8 MPa which is three order higher than PS complex.

Voltage stability

The ESW or voltage window is obtained by the linear sweep voltammetry technique (LSV). This gives the optimum stability range of voltage for application in solid-state batteries. In this technique, final residual current after polarization is recorded as a function of voltage. Initially, there is constant current, and after some time the rapid increase in current is seen this tells us the maximum working voltage for an electrolyte beyond which decomposition of the sample occurs. I/V characteristics so obtained gives us the voltage window for working range of electrolyte by plotting an intercept at sharply rising current on voltage axis [214]. Leo et al, [213] reported the lithium ion conducting CPE based on (PEO)₈-LiCF₃SO₃ dispersed with a glass-ceramic (Li_{1.4}(Al_{0.4}Ge_{1.6})(PO₄)₃) as a filler. The maximum operating voltage range obtained was 3.75 V.

Fig. 33 I Variation of residual electronic current as a function of applied dc voltage (I/V characteristics) of PNC films ((PAN)₈LiCF₃SO₃ + x (wt.%) DMMT) with various clay concentration (after ref. [84]). II I/V characteristics of PNC films based on (PAN)₈-LiPF₆ + x (wt.%) DMMT (reprinted with permission from [83], copyright Springer 2012)



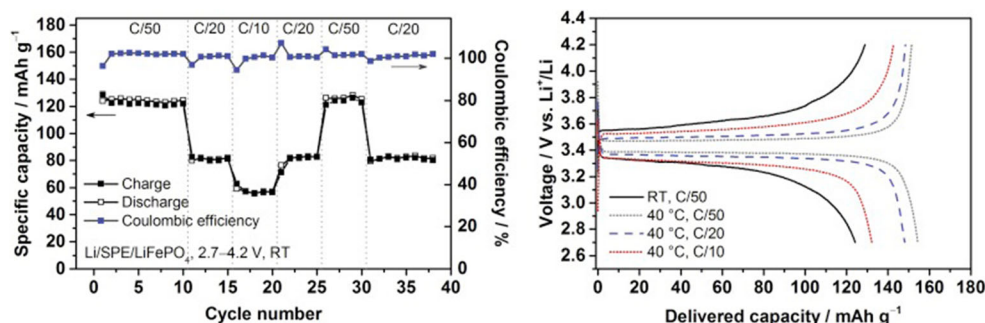


Fig. 34 Charge/discharge capacities and coulombic efficiencies for a Li/SPE/LiFePO₄ cell with the 80:20 electrolyte, cycled at room temperature (left) and initial charge/discharge voltage curves comparing Li/SPE/

LiFePO₄ cells with the 80:20 electrolyte cycled at different temperatures and C rates (right) (reprinted with permission from [215], copyright Elsevier 2015)

Li et al. [208] reported the preparation of nanofibrous membranes based on PVdF doped with ion complex (SiO₂-PAALi) by electrospinning technique. LSV shows improvement in ESW from 4.75 V to 5.05 V on the addition of SiO₂/PAALi ion complex and is sufficient for us in Li ion battery. Lee et al. [168] reported a composite electrolyte formation using PEO-PVdF + LiCO₃ and BaTiO₃ as nanofiller. Electrochemical stability window obtained from cyclic voltammetry is 4.7 V for 15 wt.%. LSV shows a broad potential window of 4.5 V for PEO-LiTf-EC as reported by Mejia et al. [78]. One report by Sharma et al. [84] shows a stability window of 5.6 V as shown in Fig. 34 (I) for PNC films. LSV study for PAN-LiPF₆ + DMMT demonstrates the enhancement in potential stability window of pure PS complex (3.2 V) to 4.3 V for PNC film for 7.5 wt.% clay concentration and decreases with high filler content due to the rapid increase in current (Fig. 34 (II)) [83]. Linear sweep polarization for PVdF-HFP-based gel polymer electrolyte shows the ESW of the order of 4.6 V as reported by Yang et al. [50]. The electrochemical stability window of polymer electrolyte for PEO-PMMA-LiTFSI-Al₂O₃ electrolyte increases from 4 to 4.6 V as measured by LSV, and it confirms the potential of electrolyte for application in Li-ion battery [81]. Janakiraman et al. [167] prepared electroactive separator based on PVdF-NaClO₄ + EC/DEC with DMSO as the solvent and the electrochemical stability window is approximately 4.3 V.

Electrochemical property analysis

Charging/discharging study

Ramesh et al. [210] observed the discharge capacity for LiNi_{0.8}Co_{0.2}O₂/PVC-PEO-LiCF₃SO₃-DBP-EC/SiO₂/MCMB cell at 1st cycle is about 50 mAh g⁻¹. Further analysis shows that discharge time and the nominal voltage of cell decreases with cycling, which leads to a reduction in discharge capacity values. Mindemark et al. [215] studied the incorporation of carbonate repeating units in a poly(ε-caprolactone) (PCL) backbone used as a host material in SPEs. Battery cycling was done for 2.7–4.2 V, and the capacity retention was found to be excellent with no significant loss in capacity over >70 cycles (Fig. 35) as well as coulombic efficiencies close to 100%.

Prasanth et al. [35] investigated the effect of PEO on electrochemical properties of electrospun PVdF-based PEs studied. The cycling performance of the Li/LiFePO₄ cells with GPE was done and it was seen that after 50 cycles, the cells with PVdF/PEO polymer blend membranes shows a discharge capacity of 162 and 152 mAh g⁻¹, respectively for LiTFSI and LiClO₄. But with cell comprising of PVdF only delivers a discharge capacity of 128 mAh g⁻¹. This decrease in discharge capacity may be attributed to the decomposition of the electrolyte. Also, capacity retention for the former cell is 95% and for the later one only 86%. It concludes that electrospinning technique can be used for the preparation of

Fig. 35 Charge and discharge profile of Na_{2/3}Co_{2/3}Mn_{1/3}O₂ half cell under 0.1 C rate, between the potential 1.25–4.3 V, a liquid electrolyte (1 mol L⁻¹ NaPF₆ in EC/PC = 1:1 (v/v)) tested under room temperature, b TiO₂-blended CPE tested under 60 °C (reprinted with permission from [216], copyright Elsevier 2015)

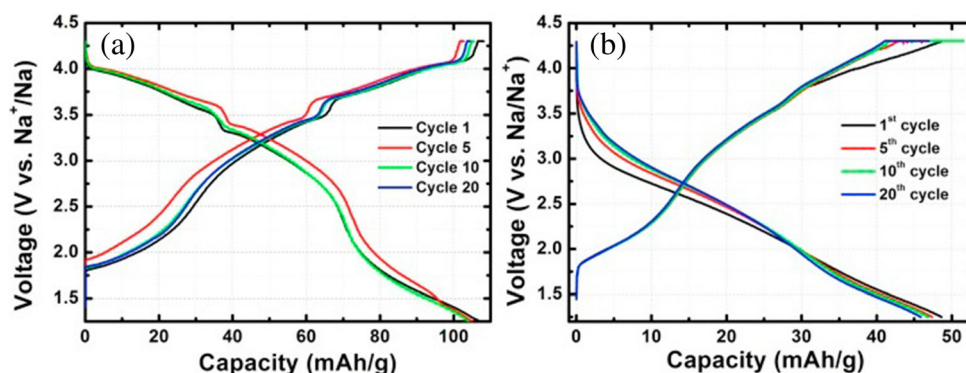
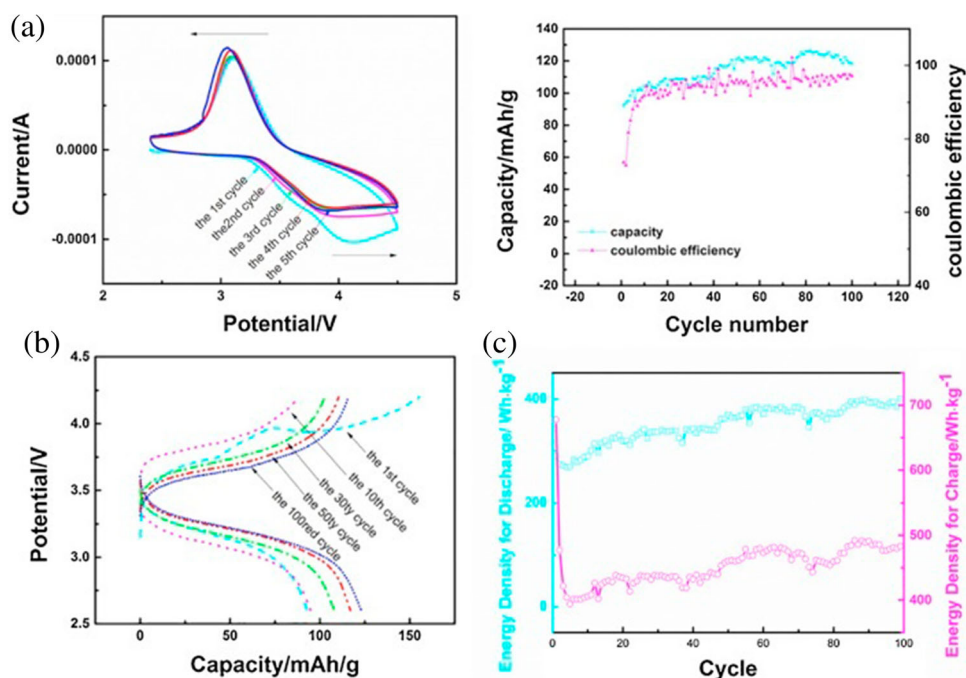


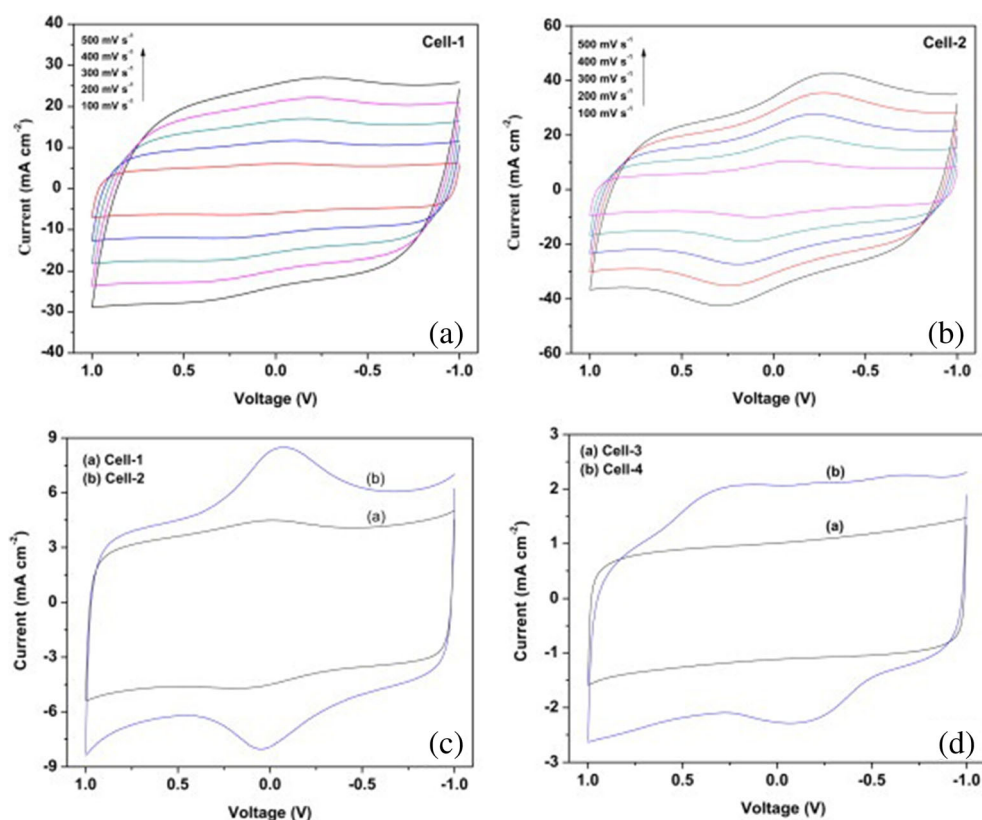
Fig. 36 Cycle property of Li/PVDF-PVA-MMT CSPE/LiFePO₄ cell: **a** cyclic voltammetry (CV) curves during the initial five cycles; **b** charge and discharge properties of Li/PVdF-PVA-MMT CSPE/LiFePO₄ cells at 0.1 C; **c** energy density for discharge (Wh kg⁻¹) and energy density for charge (Wh kg⁻¹) (reprinted with permission from [155], copyright Elsevier 2016)



CPE for energy storage devices. Mejia et al. [78] extracted a study of electrochemical properties based on PEO/lithium trifluoromethanesulfonate (LiTf)/EC/sepiolite extruded composite electrolytes. Galvanostatic charge-discharge study shows an initial discharge capacity of 142 mAh g⁻¹ and after

30th cycle, a stable capacity of 115 mAh g⁻¹ is observed with a coulombic efficiency of 95.5% and make it suitable for application purpose. Nimah et al. [216] reported preparation of SPE with PEO as the host polymer, LiClO₄ as salt and TiO₂ as nanofiller. The galvanostatic measurement study was done

Fig. 37 Cyclic voltammetry (CV) curves of supercapacitor cell 1 (a) and cell 2 (b) at different scan rates. CV curves of the supercapacitor cells with t-MWCNT electrodes (c) and p-MWCNT electrodes (d) at scan rate of 50 mV s⁻¹ for direct comparison (reprinted with permission from [209], copyright Elsevier 2013)



by cycling in the potential range of 1.25–4.3 V at the current rate of 0.1 C and 60 °C (Fig. 36). Capacity increase with the addition of nanofiller and cycle stability is up to 25 cycles. The Li/PVdF-PVA-MMT CSPE/LiFePO₄ cells show pretty high specific discharge capacity above 123 mAh g⁻¹ along with a coulombic efficiency of 97.1% after 100 cycles as shown in Fig. 27 [152].

Cyclic voltammetry

Pandey et al. [209] studied a GPEs based on LiPF₆/IL/PVdF-HFP for supercapacitor application. The supercapacitor studies were done by CV in voltage range 1.0 to 2.0 V at a scan rate of 50 mV s⁻¹ (Fig. 37) and modified MWCNT electrodes show specific capacitance value 127 F g⁻¹ with IL/LiPF₆ containing GPEs as compared with that with only IL-containing gel polymer electrolyte with value 76 F g⁻¹. Arof et al. [171] prepared polymer electrolyte with PAN as polymer host and LiBOB as salt. Cyclic voltammetry analysis shows a stability window of 1.6 V when PE used as a supercapacitor. The capacitance value is higher than that from CV and galvanostatic charge–discharge tests, which are 24 and 22 F g⁻¹, respectively.

Conclusions

A detailed critical review of the PEs (published over the last three decades) used in electrochemical devices has been discussed and analyzed properly. The different sample preparation techniques and sample methodology have been examined in details. The selection criterion for the host polymer (such as PEO, PAN, PVdF, PEMA, PVC, PVA, etc.), appropriate salt (LiPF₆, LiClO₄, NaPF₆, LiCF₃SO₂, etc.), aprotic solvents (methanol, acetone, acetonitrile, etc.), and fillers clays (YZO, CeO₂, lithium/sodium montmorillonite, etc.) have been addressed properly. A detailed ion transport mechanisms for lithium ion transport like VTF, WLF, free volume theory, dispersed/intercalated mechanisms, etc., in polymer electrolysis are reviewed and analyzed. The fillers/clays have been used for enhancing the properties like ionic conductivity, surface structure/microstructure, electrochemical, stability, etc. The reduction in crystallinity with the addition of filler/clay is observed. Out of a large number of published reports, it has been concluded that solid polymer electrolytes are the suitable candidate for commercial applications due to simultaneously improved properties such as mechanical strength, voltage stability window, mechanical flexibility, and thermal stability over liquid and gel polymer electrolytes. Now, a thin/safe/flexible/low-cost electrolyte cum separator is claimed for electrochemical devices, and it can be accomplished by using solid polymer electrolytes cum separators.

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