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Ionic Liquid-Based Gel Polymer Electrolytes for Application in Rechargeable Lithium Batteries

Himani Gupta and Rajendra K. Singh

Abstract

Depleting fossil fuels has put pressing need for the search of alternative energy resources. Solar and wind energy resources are being considered one of the viable solutions. However, these intermittent sources require efficient energy storage systems in terms of rechargeable Li batteries. In Li batteries, electrolyte is one of the most important components to determine the performance, as it conducts the ions between the electrodes. In battery, mostly liquid electrolyte is used as it shows high ionic conductivity and electrode/electrolyte contact which help to reduce the internal resistance. But these are not electrochemically very stable and raised some major problems such as reactivity with electrode, dissolution of electrode ions, leakage, volatility, fast Li dendrite growth, etc. Therefore, in order to improve its electrochemical performance, selection of electrolyte is an important issue. In the present study, ionic liquid (IL)-based polymer electrolyte is used over liquid electrolyte in which IL acts as a plasticizer and improves ionic conductivity and amorphicity. These electrolytes have high thermal and electrochemical stability, therefore, can be used in high voltage Li battery. Also, their mechanical stability helps to suppress Li dendrites growth. Therefore, polymer electrolytes can open a new way in the progression of battery application.

Keywords: ionic liquid, polymer electrolyte, ionic conductivity, electrochemical analysis, Li battery

1. Introduction

Energy contributes a major role in various aspects of human life and their demand is continuously increasing with time. To meet this challenge, world population mostly depends on fossil fuels which include petroleum, coal, nuclear power and natural gases. But the climate change due to the frequently increasing CO₂ level has driven the research in the development of renewable energy sources. Research in the field of renewable energy sources such as solar energy, wind energy and hydropower has been initiated but the major problem to efficiently utilize these energies is to investigate suitable electrical energy storage devices because these energy sources are intermittent in nature. For this purpose, the most efficient energy storage devices are the batteries and super capacitors [1, 2]. Both the devices have their own importance depending on usage but batteries are continuing to dominate in the market of portable electronic system because of their

high energy density and voltage rating [3]. Battery is an electrochemical device which can convert chemical energy into electrical energy through redox reaction to release the energy. Conversely, it can also convert electrical energy into chemical energy to store the energy. Among all the batteries, rechargeable lithium batteries (Li-batteries) are gaining much attention in the electric power storage system due to their high capacity, working voltage, long lifetime, low self-discharge rate and no memory effect (**Figure 1**) [4, 5]. However, the energy density of recent Li batteries is in the range of 100–200 Wh/Kg which limits their use in automotive application [6]. Therefore, to enhance their energy density, Li metal is frequently used because it shows very high capacity for Li battery. Metallic lithium as anode is being used since long time but its application with organic liquid electrolytes arises the main issue in lithium batteries as lithium dendrite growth [7–9]. Further, the use of these volatile and flammable electrolytes causes safety problems during cycling. Also, these organic liquid electrolytes cannot be used in high voltage batteries due to their electrochemical instability at higher voltage [10].

Therefore, for safely utilization of Li metal in batteries, requirement of alternative electrolyte is highly demanded. In this context, polymer electrolytes are gaining much attention in Li batteries because of their outstanding properties such as mechanical, thermal and electrochemical stability, safety and flexibility [11, 12]. The polymer acts as a host matrix for ion movement in which ions can move in the free space provided by the polymer matrix. Generally, solid polymer electrolytes (SPEs) are formed by dissolving organic salt into the polymer matrix. The selection of polymer matrix mainly depends on the presence of polar group so that it can easily coordinate with the cations; and there is less restraint in the bond rotation [13]. Among the different polymer matrices, poly (ethylene oxide) (PEO) based polymer electrolytes are mostly studied due to its high chain flexibility and ability to dissolve different organic/inorganic materials [14, 15]. However, PEO based solid electrolytes are semi-crystalline in nature which comprise the crystalline and

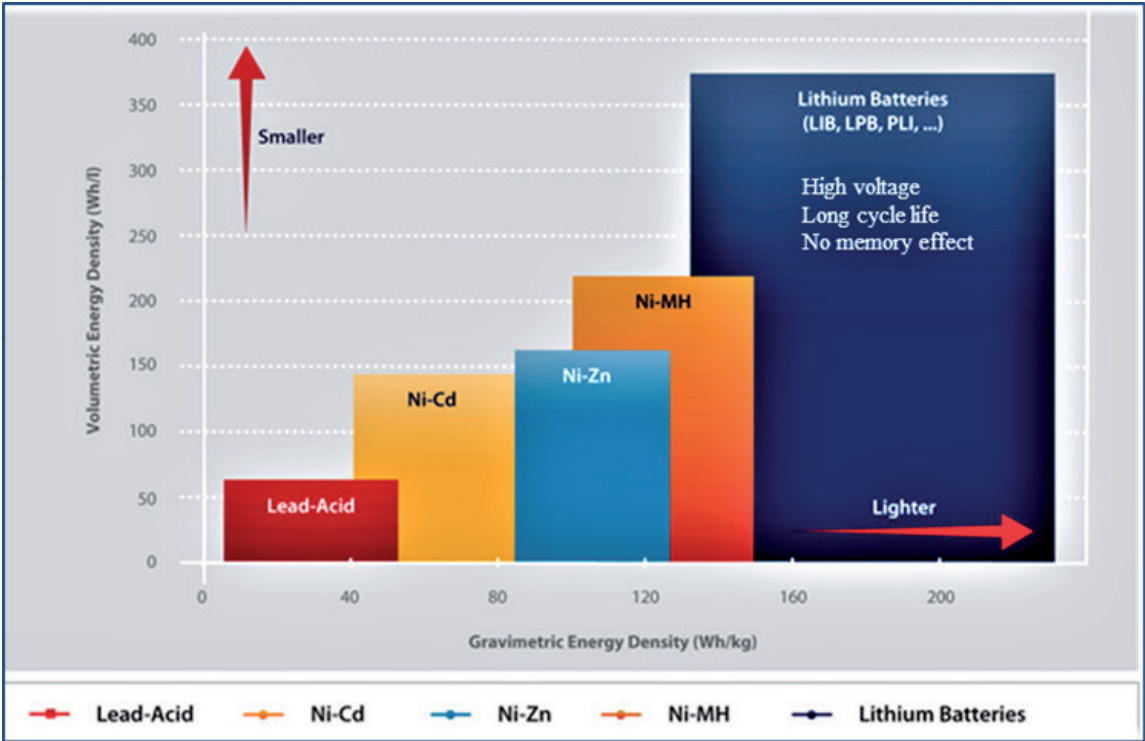


Figure 1.
Comparison in different types of batteries.

amorphous regions both; and it is reported that the ion conduction in polymer electrolytes occurs only in amorphous region [16–18]. Therefore, they show lower room temperature ionic conductivity (10^{-8} to 10^{-6} S/cm) and hence cannot be used in practical battery application. To overcome this drawback and to obtain polymer electrolytes having good ionic conductivity, flexibility, mechanical and electrochemical stability, different approaches are reported such as the addition of nanofillers, use of plasticizers or gel polymer electrolytes (GPEs) [19, 20]. Among these approaches, use of GPEs is in focus as they combine the desirable properties of both liquid (high conductivity) as well as solid (mechanical stability). Thus it is a suitable replacement of electrolyte for high performance batteries. In the present chapter, fundamental properties of PEO based polymer electrolytes; their classifications and performance in Li batteries are discussed.

2. Properties and ion transport mechanism in PEO

PEO has chemical structure $\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$ which is a polyether compound. Depending on the molecular weight of polymer, it is also known as polyethylene glycol (PEG). Generally, polymer having molecular weight above 20,000 g/mol is called PEO while, below 20,000 g/mol is known as PEG [21]. PEO is a low toxic compound; therefore, it is widely used in many applications such as chemical, industrial, medical, biological etc. PEO has ethylene oxide unit which provides flexibility and high donor number for Li^+ ions and promotes the ion transport. Also, it has high dielectric constant and Li^+ ion solvating ability [22]. The ion transport mechanism in PEO occurs by the coordination of Li^+ ions with the ether oxygen atom of PEO chain. This process occurs by formation and dissociation of $\text{Li}-\text{O}$ bond by local segmental motion of polymer chain (Figure 2) [23]. The ion transportation in polymer

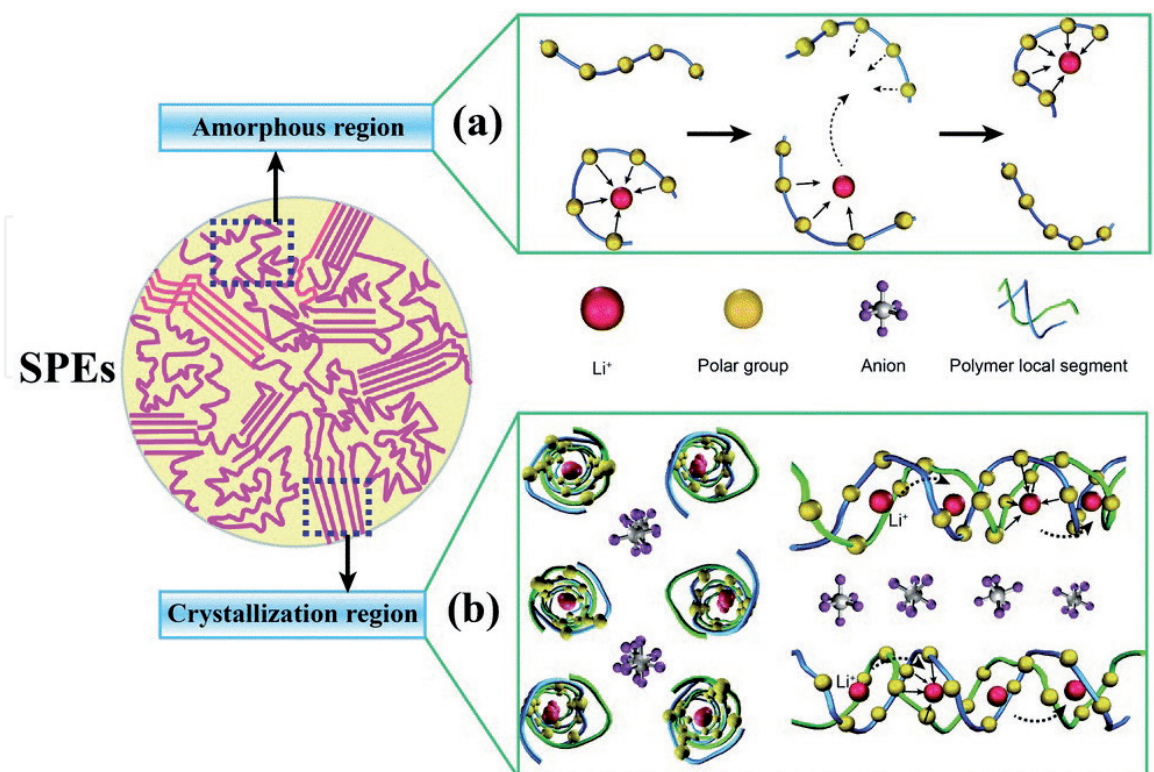


Figure 2.
 Ion transport mechanism in polymer PEO in (a) amorphous as well as (b) crystalline region.

electrolytes mainly depends on polymer chain segmental motion which becomes faster in amorphous region or above the glass transition temperature (T_g) of polymer (as shown in **Figure 2(a)**). Hence, ideally polymer should have lower T_g to remain in rubbery state or to promote the Li^+ ion conductivity at RT [17]. In order to enhance Li^+ ion conductivity of polymer electrolytes different strategies such as addition of nano fillers, use of plasticizers or gel polymer electrolytes has been proposed. On this basis, polymer electrolytes are classified into different categories as discussed below.

3. Classification of polymer electrolytes

Polymer electrolytes are considered to be promising materials in the research and development of electrochemical devices. On the basis of materials, polymer electrolyte is classified into following categories (**Figure 3**):

3.1 Dry solid polymer electrolytes

It is formed by incorporating inorganic salt into the polar polymer thus ion conducting electrolyte is known as solid polymer electrolyte [24]. The electrostatic interaction between the metal ions of salt and polar polymer results the formation of coordination bond. This metal-polymer interaction can be affected by many factors such as nature and distance between the functional group of polymer, molecular weight, nature of branching, charge on metal and counter ion [25]. When the polymer electrolyte is placed in the electric field, ions start to move from one coordination site to other. It occurs due to weaker interaction between the metal ion and functional group of polymer chain.

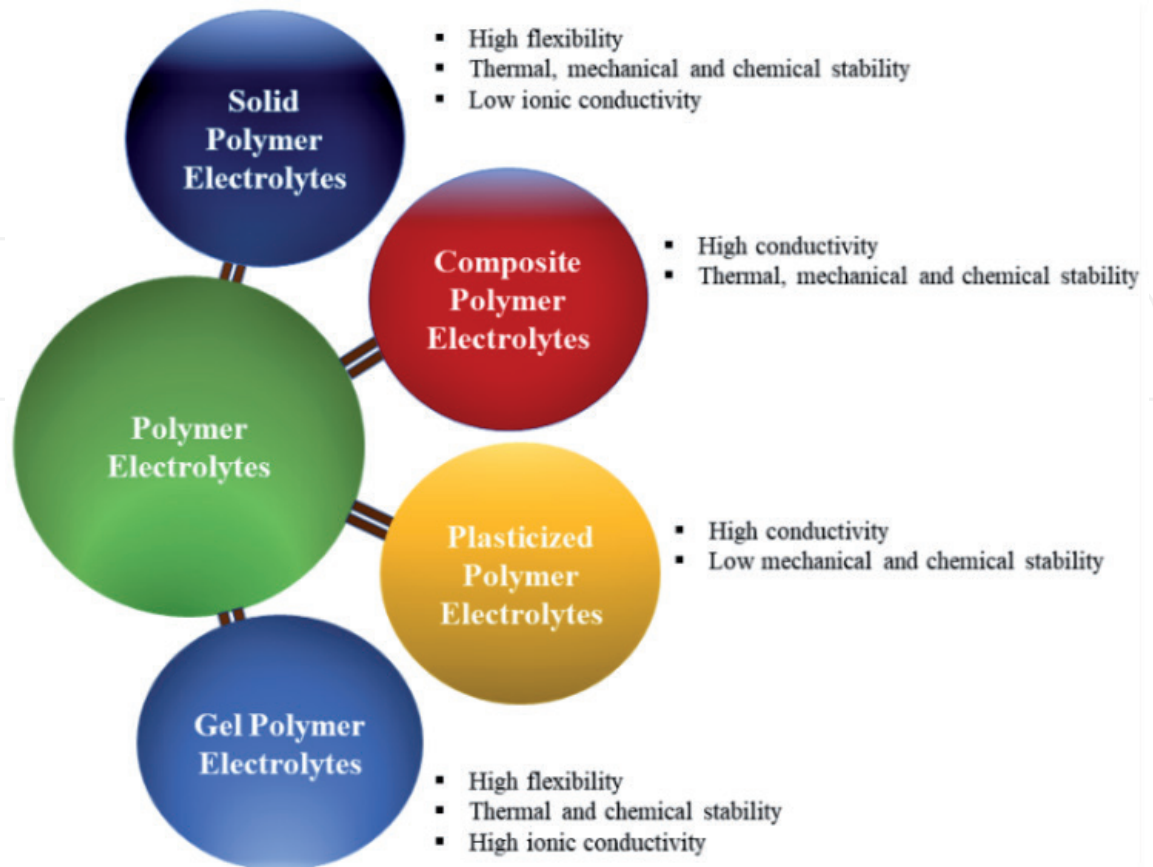


Figure 3.
Differently types of polymer electrolytes used in Li battery.

3.2 Plasticized polymer electrolytes

Plasticized polymer electrolytes are formed by dissolving low molecular weight compounds (e.g. ethylene carbonate (EC), propylene carbonate (PC), poly ethylene glycol (PEG)) [26]. These plasticizers reduce the inter and intra-molecular interaction between the polymer chain, thus reduce the T_g and crystallinity of polymer chain and enhance the salt dissociation ability [27]. Although this approach improves the conductivity of polymer electrolyte, but it also provides low mechanical stability, solvent volatility and reactivity with lithium electrode.

3.3 Composite polymer electrolytes

Conductivity of polymer electrolytes also decreases due to the presence of ion pair formation. This behavior is observed mainly because of the low dielectric constant of polymer matrix [28]. To overcome this issue, high dielectric constant inorganic inert fillers (such as TiO_2 , SiO_2 , etc.) are dispersed into the polymer electrolyte to avoid ion-ion association. The obtained electrolyte combines the properties of ceramic fillers as well as polymer and results the flexible, mechanically stable composite polymer electrolyte [29].

3.4 Gel polymer electrolytes

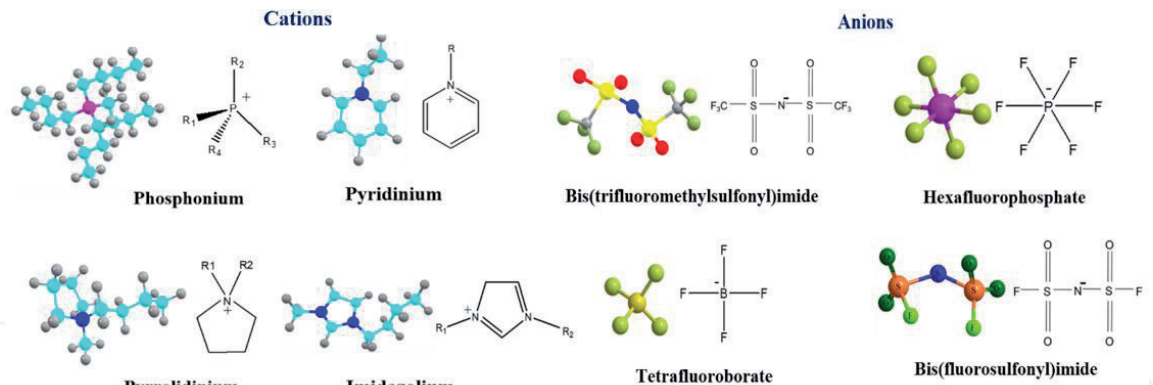
In all the polymer based electrolytes, gel polymer electrolytes (GPEs) are focusing much attention because they combine the advantages of liquid electrolyte such as high conductivity, good electrode/electrolyte contact and solid electrolytes like as safety, mechanical and thermal stability. In GPEs, polymer is used to trap the liquid constituent and provides mechanical support, thus it is considered as safer than liquid electrolytes. For the synthesis of GPEs, large amount of organic solvent is used in the polymer in which its conduction takes place along the host polymer [30]. Recently, ionic liquid (IL) based GPEs are in focus of the research due to the desirable properties of ILs such as high conductivity, thermal stability, negligible vapor pressure which makes GPE as a suitable replacement of liquid electrolyte.

4. Ionic liquid

ILs are the molten salts that remain in liquid state below $100^\circ C$. Sometimes these are also referred as room temperature molten salts, ionic fluids, fused salts or organic salts. ILs are generally formed by self-dissociated, poorly coordinated, bulky organic cations and organic/inorganic anions [31]. Some of the common cations and anions of ILs are given in **Figure 4**. These ILs do not have strong ionic bond between the cations and anions as in ionic salts ($NaCl$, KCl , etc.), hence possess low lattice energy and remain in dissociated state. Therefore, they show many desirable properties as high conductivity, low vapor pressure, melting and glass transition temperature, high thermal and electrochemical stability, less polluting and easily recyclable [32]. Some of the properties of ILs are given in **Table 1** [33–35].

4.1 IL based gel polymer electrolytes

ILs provide outstanding ionic conductivity upto the decomposition temperature which enable them to be used as electrolyte. Also, to eliminate their leakage issue, ILs are trapped in polymer matrices which are known as GPEs. These IL based GPEs show high conductivity, good thermal and electrochemical stability, transparency and flexibility (**Figure 5**) [36].



ILs based GPEs	Conductivity (mS/cm)	References
PEO ₂₀ LiTFSI ₂ [Pyr _{1,20} TFSI] ₄	2.5 × 10 ⁻⁴ at 20°C	[37]
PEO ₂₀ LiTFSI ₁ [Pyr _{1,20} TFSI] _{1.5}	7 × 10 ⁻⁵ at 20°C	[35]
PVdF-HFP + 20 wt.% LiTFSI+60% BMIMBF ₄	1.7 at RT	[38]
PPEGDA ₁₅ %[LiBF ₄ Im ₁₂ BF ₄] ₈₅ %	1.2 × 10 ⁻⁴ at 20°C	[39]
[PPyr ₁₁ TFSI] ₅₀ %[Li(G ₄)]TFSI ₅₀ %	1 × 10 ⁻⁴ at 20°C	[40]
EGDMA-MMA + 0.5 M PP ₁₄ Cl + 80% PP ₁₄ TFSI	0.09 at 25°C	[41]
PEO + 20wt%LiFSI+7.5wt%EMIMFSI	0.289 at RT	[36]
PEO + 20wt%LiTFSI+12.5wt%EMIMTFSI	0.208 at 30°C	[42]
PEO ₂₀ LiTFSI [Pyr ₁₃ TFSI] _{2,15}	3 × 10 ⁻⁴ at 20°C	[43]
PEO + 10wt%NaMS+60wt%BMIM-MS	0.105 at 30°C	[44]
PEO + 10% NaTFSI+40% BMIMTFSI	0.4 at 30°C	[45]
PEO ₂₀ LiTFSI ₂ [Pyr ₁₄ TFSI] ₂	1 × 10 ⁻⁴ at 20°C	[46]

Table 2.
Ionic conductivity of ILs based GPEs.

5. Results and discussion

5.1 Surface morphology and crystallinity of IL based GPEs

The effect on surface morphology and degree of crystallinity of PEO based SPE with the addition of IL is reported in literature. Gupta et al. [47] studied that, by using the phosphonium based IL (Trihexyltetradecylphosphonium TFSI) in polymer electrolyte (PEO + 20 wt% LiTFSI), increment in amorphous region was obtained (**Figure 6**). The surface morphology of PEO based GPE is given in **Figure 6**. **Figure 6(a)** shows the crystalline region of polymer PEO, when IL (up to 20 wt%) was incorporated into PEO-LiTFSI system, smoother morphology was observed which resulted the amorphous nature of GPE. Singh et al. [48] also reported that the suppression in rough surface nature of polymer electrolyte (PEO + 20 wt% LiTFSI) was observed when BMIMTFSI IL was added into it. The smoother surface morphology of polymer electrolyte was observed due to the plasticization effect of ionic liquid which reduced the interaction between the polymer chain and made it more flexible.

From the XRD analysis, crystallinity of GPEs is also reported in many studies. Gupta et al. [47] reported the variation in crystallinity of SPE with the addition of phosphonium based IL They showed the semi-crystalline nature of polymer PEO. When LiTFSI salt and IL were added into the PEO, broadening of halo region and FDHM of polymer electrolytes were noticed which resulted the decrement in crystalline region or enhancement in amorphous region of polymer electrolyte (**Figure 7(A)**).

Singh et al. [48] reported the effect of BMIMTFSI IL on the crystallinity of SPE (PEO + 20 wt% LiTFSI). They showed that with the addition of IL into SPE, halo region was increased substantially and relative intensities of the crystalline peaks reduced. This proved the enhancement in amorphous phase in polymer electrolyte (**Figure 7(B)**). Therefore, presence of IL in polymer electrolyte improves its amorphous region which is desirable for the conduction of Li⁺ ions, since, conduction in polymer electrolytes occurs only in this region.

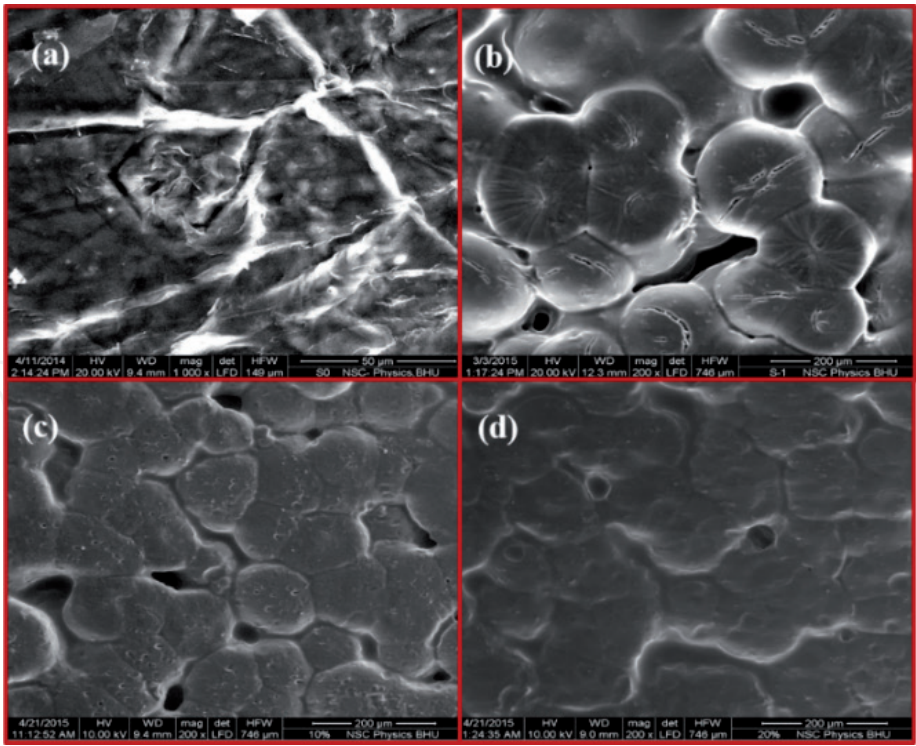


Figure 6.
SEM image for (a) pure PEO and PEO + 20 wt% LiTFSI + X wt% IL (b) $X = 0$, (c) $X = 10$, (d) $X = 20$.

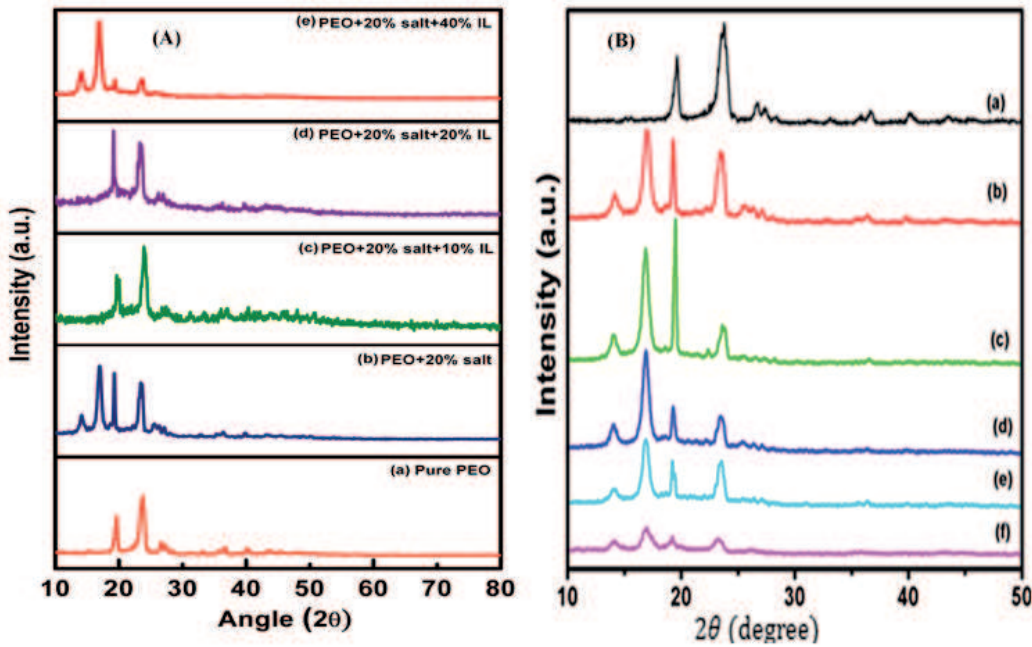


Figure 7.
XRD pattern of (A) phosphonium IL based polymer electrolytes, PEO + 20wt.%LiTFSI + x % IL ($x = 0, 10, 20, 40$); and (B) polymer electrolytes (a) PEO with PEO + 20wt.%LiTFSI + x wt.% BMIMTFSI (b) $x = 0$, (c) $x = 5$, (d) $x = 10$, (e) $x = 15$ and (f) $x = 20$.

5.2 Ionic and Li^+ ions conductivity of IL based GPEs

In batteries, electrolyte plays the major role to transport the ions between the two electrodes. So, conductivity of electrolyte is very important parameter for Li battery. It is well known that the IL acts as a plasticizer and its presence in polymer electrolyte enhances the ionic conductivity. IL also provides free charge carriers and therefore helps to promote the ionic conductivity of polymer electrolyte.

The increment in the conductivity of polymer electrolyte with IL concentration is also reported by Gupta et al. [49] and Balo et al. [36] which are depicted in **Figure 8(a)** and **(b)** respectively. Gupta et al. [49] showed that ionic conductivity of polymer electrolyte (PEO + 20 wt% LiFSI) increases with IL (PYR₁₃FSI) concentration.

Whereas, Balo et al. [36] synthesized the PEO based polymer electrolyte (PEO + 20wt.%LiFSI + xwt.%EMIMFSI; for 0 ≤ x ≤ 15) and mentioned the use of optimized concentration of IL in polymer electrolyte. They found similar increasing trend of conductivity of polymer electrolyte with IL, but after certain concentration, it showed decreasing trend (**Figure 8(b)**). It happened because with the addition of IL into polymer electrolyte, large number of FSI⁻ anions was available which started to interact with Li⁺ ions present in the polymer electrolyte. Therefore, they formed ion pairs instead of participating in interaction with ether oxygen of PEO, due to which conductivity of electrolyte was reduced.

5.3 Electrochemical stability of IL based GPEs

Electrochemical stability of electrolyte is an important parameter as it decides the performance of the battery in working voltage range. Electrochemical stability of GPEs should be high so that it can be used in high voltage Li batteries. Many studies have been carried out on the electrochemical performance of PEO and IL

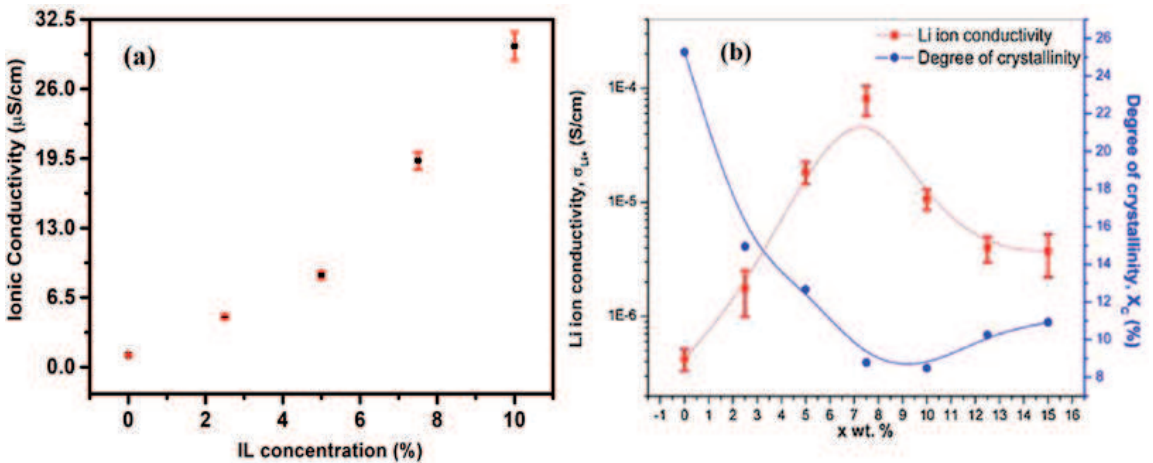


Figure 8. Variation in (a) ionic conductivity as well as (b) Li⁺ ion conductivity and degree of crystallinity of polymer electrolyte with IL concentration.

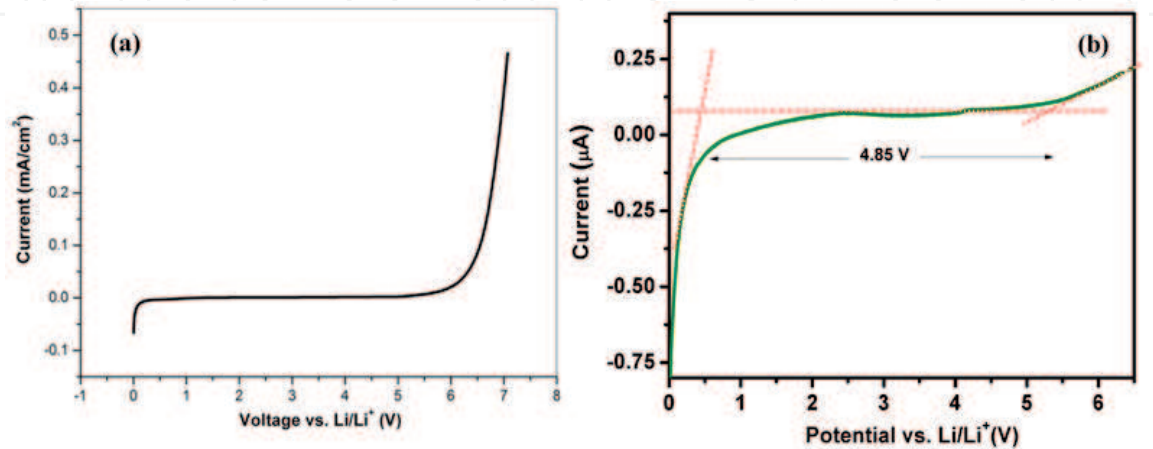


Figure 9. Electrochemical stability of (a) imidazolium (EMIMFSI) and (b) pyrrolidinium (PYR₁₃FSI) IL based GPEs.

based GPEs. Singh et al. [48] synthesized the GPE, PEO + 20 wt% LiTFSI + xwt% BMIMTFSI ($x = 5, 10, 15, 20$) for Li battery and the electrochemical stability of 20 wt% IL containing GPE was reported ~ 4 V vs. Li/Li⁺.

Balo et al. used the same polymer system with EMIMFSI and EMIMTFSI ILs and found that the GPE, PEO + 20 wt% LiTFSI + 10 wt% EMIMFSI was electrochemically stable up to ~ 6.4 V vs. Li/Li⁺ (**Figure 9(a)**) [50]. In another study they showed that the polymer electrolyte, PEO + 20 wt% LiTFSI + 10 wt% EMIMTFSI, was stable upto ~ 5.1 V vs. Li/Li⁺ [42]. Also, Gupta et al. [49] reported the electrochemical stability of pyrrolidinium IL based GPE (PEO + 20% LiFSI + 10% PYR₁₃FSI) which was ~ 4.8 V vs. Li/Li⁺ (**Figure 9(b)**). Therefore, it can be concluded that IL based GPEs show enough electrochemical stability to be used in high voltage Li batteries application.

6. Application of IL based GPEs in Lithium batteries

Because of having several required properties, IL based polymer electrolytes are frequently used in many application as in supercapacitors, batteries and fuel cell etc. Particularly, in Li batteries, they are gaining much attention due to their high energy density, flexibility and safety. In recent years, almost all the electronic equipment are being run by polymer batteries as laptop, mobile phones, power banks, portable media players etc. Many reports include the application of GPEs in Li batteries. As one of the main advantage of GPE is that it forms stable solid electrolyte interface (SEI) passive layer between the electrode-electrolyte and provides higher cyclic stability to Li battery. Battery performance of PEO based GPEs have already been studied in literature. Gupta et al. [51] synthesized the GPE, (PEO + 20 wt% LiTFSI + 30 wt% 1-butyl-3-methyl pyridinium TFSI), and reported its performance in Li battery in (Li/LiFePO₄) configuration. They obtained maximum discharge capacity ~ 160 mAh/g and 99% Coulombic efficiency upto 35 cycles at 40°C (**Figure 10(a)** and **(b)**). In another report, they used the pyrrolidinium based IL in polymer system, PEO + 20% LiFSI + 10% PYR₁₃FSI, with graphene oxide coated LiFePO₄ cathode and obtained maximum discharge capacity ~ 163 mAh/g at C/10 rate at room temperature (RT) (**Figure 10(c)**) [49]. It was the result of high conductivity of IL, PYR₁₃FSI and LiFSI salt as well as high electronic conductivity and large surface area of graphene oxide (GO) which enhanced the electron transfer rate and hence capacity of Li battery. This Li battery provided almost constant capacity and Coulombic efficiency upto 100 cycles (**Figure 10(d)**). Balo et al. [36] reported the same system (Li/LiFePO₄) using imidazolium IL based polymer electrolyte PEO + 20 wt.% LiFSI + 7.5wt.%EMIMFSI at RT.

They found maximum discharge capacity ~ 143 mAh/g at C/20 rate which decreased upto 130 mAh/g at C/10 and further reduced upto 20 mAh/g at 2C discharge rate. This reduction of discharge capacity was reported due to the increase of electrolyte ohmic drop and limited Li⁺ ion diffusion in composite cathode. The above polymer systems have been also tested with high voltage and capacity cathode materials such as LiNi_xMn_yCo_zO₂ (NMC) and LiNi_xCo_yAl_zO₂ (NCA). These electrolytes are electrochemically stable even at high voltage which deliver high capacity and cyclic stability to the Li battery. Gupta et al. [52] used the phosphonium based IL (trihexyltetradecylphosphonium bis TFSI) in PEO-LiTFSI polymer system.

They fabricated the Li cell (Li/LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂) and obtained maximum discharge capacity ~ 148 mAh/g with 95% Coulombic efficiency upto 150th cycle at C/10 rate in the voltage range of 2.4–4.2 V (**Figure 11(a, b)**). The impedance of the Li cell was also evaluated with cycling (inset of **Figure 11(b)**). It showed the slight increment in the interfacial resistance value and hence, resulted very small capacity fading of Li cell (**Figure 11(b)**). Balo et al. [50] used imidazolium IL (EMIMFSI)

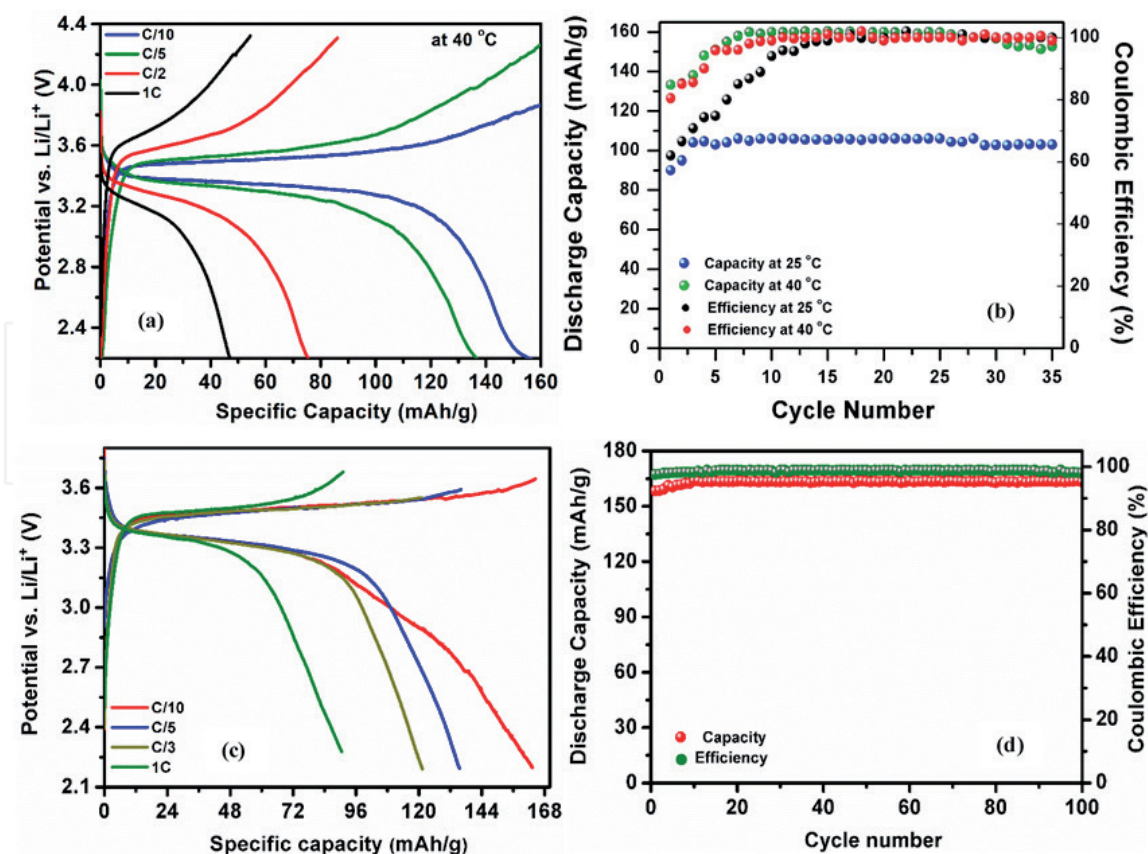


Figure 10.
 Electrochemical performance of (a, b) 1-butyl-3-methyl pyridinium TFSI and (c, d) N-propyl-N-methylpyrrolidinium-FSI IL based polymer electrolytes with Li/LiFePO₄ and graphene oxide coated LiFePO₄ cathode respectively.

based GPE (PEO + 20 wt% LiTFSI + 10 wt% EMIMFSI) in Li/NCA cell. They observed the discharge capacity ~175 mAh/g at C/10 current rate which remained almost stable throughout cycling (**Figure 11(c, d)**) and only 0.05% of total capacity was lost during 200 cycles (inset of **Figure 11(d)**). The use of Li metal electrode in Li batteries are in demand due to its higher energy density and capacity (3862 mAh/g), but it could not be frequently used in application purpose because of the formation of Li dendrites. This Li dendrite is formed due to the deposition of Li⁺ ions on the Li metal surface during cycling which starts to grow and causes short circuiting and results low cyclic stability. Therefore, in order to obtain high capacity and safer Li battery, suppression of dendrite growth is important. It was reported that the dendrite growth becomes faster with liquid solvents. But the use of GPEs in Li battery is able to suppress its growth because of having mechanical stability. Therefore, the use of GPEs provides safety and cyclic stability to Li battery. The electrochemical stability of GPEs with Li electrode is reported in literature. Wang et al. [53] reported the combination of the use of LAGP-PEO (LiTFSI) composite solid electrolyte and the modification of Li anode with PEO₅₀₀₀₀₀ (LiTFSI) in Li/LiMn_{0.8}Fe_{0.2}PO₄ battery. They obtained that the use of both can effectively prevent the Li dendrite growth. Kim et al. used three different ILs (BMITFSI, BMIBF₄ and BMICF₃SO₃) in polymer system (PEO-LiTFSI) and reported that the Polymer electrolyte with BMITFSI IL resulted low and stable interfacial resistance or dendrite growth on lithium metal. Balo et al. [50] examined the performance of EMIMFSI IL in PEO-LiTFSI system. They found the stable and uniform formation of Li dendrite between lithium and GPE during cycling (**Figure 12(a)**). They also evaluated the interfacial resistance of this passive layer and observed that except the initial few cycles almost stable interfacial resistance 380 Ω/cm² was obtained throughout the cycling (**Figure 12(b)**).

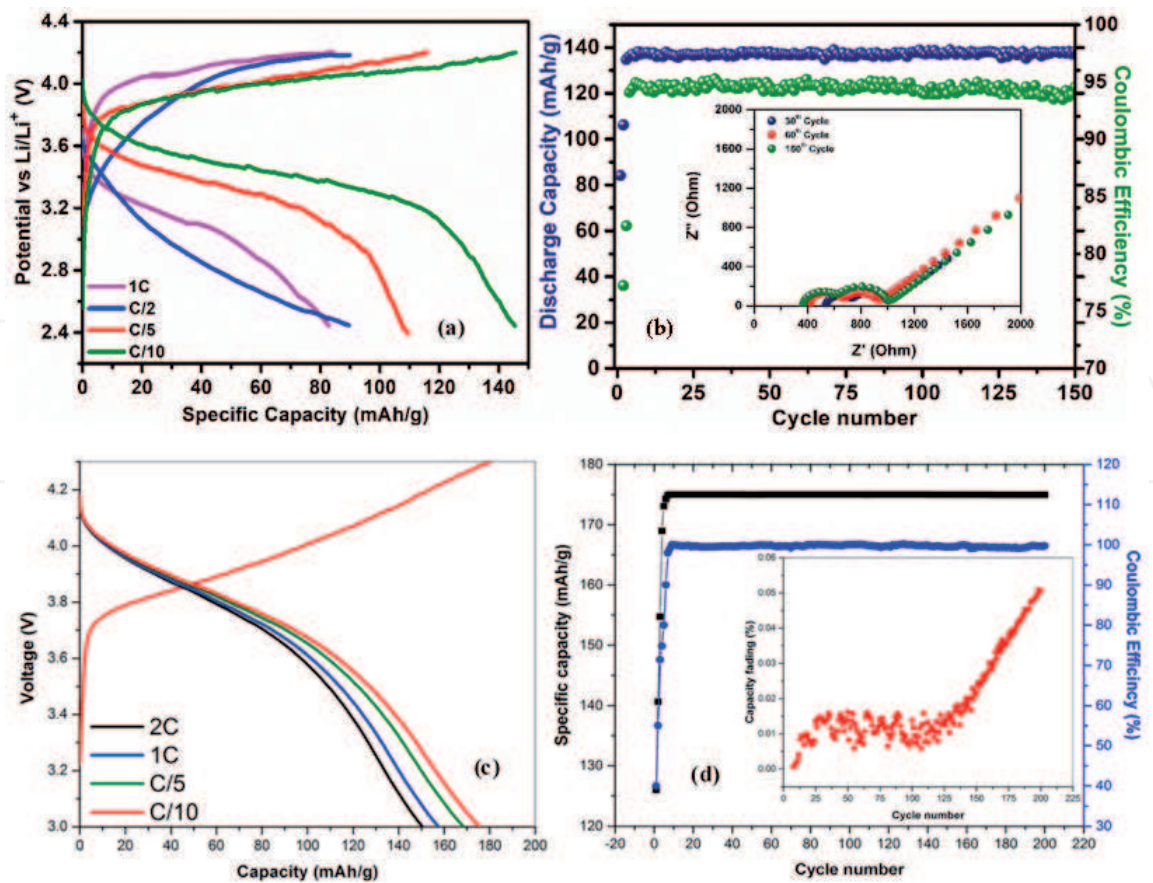


Figure 11. Discharge capacity, efficiency (at C/10 rate) and capacity fading of the Li cell (a, b) Li/ (PEO + 20wt%LiTFSI + 20wt% trihexyltetradecylphosphonium TFSI)/LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ and (c, d) Li/ (PEO + 20 wt% LiTFSI + 10 wt% EMIMFSI)/NCA.

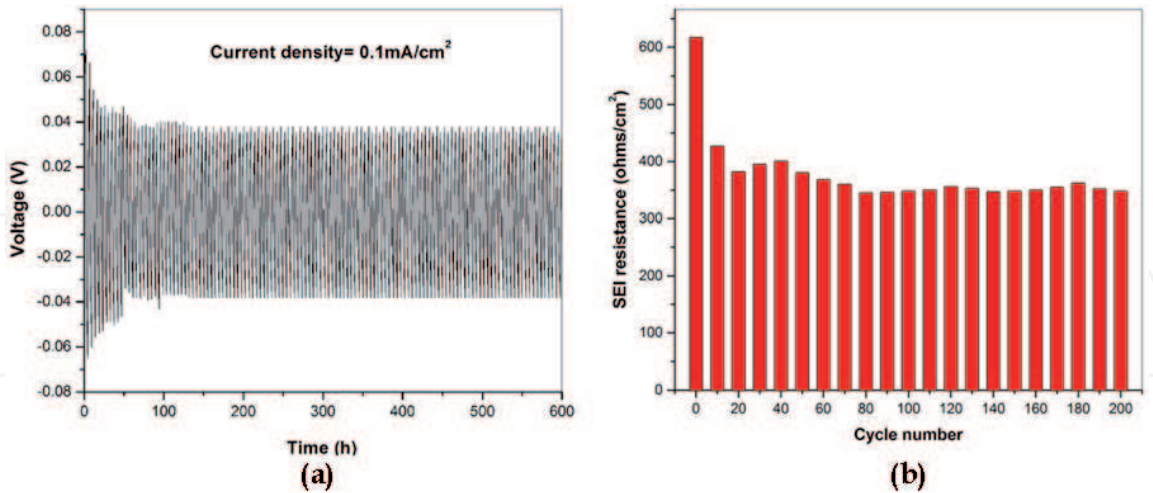


Figure 12. (a) Voltage vs. time profile of lithium deposition and (b) evolution of interfacial resistances during cycling using GPE (PEO + 20wt% LiTFSI + 10wt% EMIMFSI).

Other reports on the electrochemical performance of Li batteries using PEO based GPEs are also tabulated in **Table 3**. All these analysis shows that the use of GPEs in Li battery maintains the cyclability and electrochemical stability of the Li battery much more compared to liquid solvents.

Therefore, from the above discussions it can be concluded that the IL based GPEs not only provide good ionic conductivity, flexibility and mechanical stability but also act as a potential candidate in order to enhance the capacity, cyclicity and safety to Li battery.

Polymer electrolytes	Li battery	C-rate	Capacity (mAh/g)	References
PEO ₂₀ LiTFSI[Pyr13TFSI] _{1.27}	Li/LiFePO ₄ at RT	C/10	115 at 20 cycles	[54]
PEO ₂₀ LiTFSI ₂ [Pyr14TFSI] ₄	Li/NMC at 40°C	C/10	160 at 100th cycle	[55]
PEO ₂₀ LiTFSI[Im12TFSI]	Li/LiFePO ₄ at 50°C	C/5	110 at 20th cycle	[56]
PEO ₂₀ LiTFSI[Pip _{1.101} TFSI]	Li/LiFePO ₄ at RT	C/20	120 at 35th cycle	[57]
PEO ₂₀ LiTFSI[Pip _{1.101} TFSI]	Li/Li ₄ Ti ₅ O ₁₂ at RT	C/20	150 at 40th cycle	[57]
PEO ₂₀ LiTFSI ₂ [Pyr14TFSI] ₄	Li/LiFePO ₄ at 40°C	C/10	140 at 450th cycle	[58]
PEO + 20wt%LiTFSI + 20wt%ThdpTFSI	Li/NMC622 at RT	C/10	148 at 150th cycle	[52]
PEO ₂₀ LiTFSI ₂ [Pyr14TFSI] ₂	Li/LiFePO ₄ at 40°C	C/5	160 at 180th cycle	[59]
PEO-LiTFSI-10wt%EMIMFSI	Li/NCA at RT	C/10	175 at 200th cycle	[50]
PEO + LiFSI + 7.5 wt.% EMIMFSI	Li/LiFePO ₄ at RT	C/20	143 at 100th cycle	[36]
PEO + LiTFSI + 12.5%EMIMTFSI	Li/LiMn ₂ O ₄ at RT	C/10	120 at 10th cycle	[42]
PEO + 20%LiTFSI + 30%(1-butyl 3-methyl pyridiniumTFSI)	Li/LiFePO ₄ at 40°C	C/10	160 at 25th cycle	[51]
PEO + 20%LiFSI + 10%PYR13FSI	Li/GO-LiFePO ₄ at rt	C/10	163 at 100th cycle	[49]
PEO + 20wt%LiTFSI + 20 wt% BMIMTFSI	Li/LiMn ₂ O ₄ at RT		140 μAh/cm ² at 25 cycle	[48]

Table 3.
Electrochemical performance of Li batteries using IL based GPEs.

7. Conclusion

In summary, many approaches have been proposed to enhance the conductivity of PEO based polymer electrolyte below melting temperature. Among them, ionic liquid based GPEs are considered as the most promising approach. These GPEs enhance the ionic conductivity, thermal and electrochemical stability of the polymer electrolytes. They provide better electrode-electrolyte contact, mechanical stability and safety to Li batteries. Because of having enough mechanical stability, they are able to suppress the undesirable dendrite formation and help to provide safer Li battery. Also, due to their high electrochemical stability, they can be used in high voltage and energy density batteries. In these batteries, they show good electrochemical and cyclic stability as well as offer flexibility and safety. Therefore, these IL based GPEs can be considered as a potential candidate for replacement of liquid electrolyte in Li batteries.

Acknowledgements

One of the authors (RKS) thankfully acknowledges the financial support by DST-SERB, New Delhi, BRNS-DAE to carry out the research work. H. Gupta is grateful to DST, India for providing SRF project fellowship.

Conflict of interest

The authors declare no conflict of interest.

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References

- [1] Kim BK, Sy S, Yu A, Zhang J. Electrochemical supercapacitors for energy storage and conversion. *Handbook of Clean Energy Systems*. John Wiley & Sons, Ltd.; 2015:1-25. DOI: 10.1002/9781118991978.hces112
- [2] Monzer AS, Gualous H, Omar N, Mierlo JV. Batteries and supercapacitors for electric vehicles. *New Generation of Electric Vehicles*. InTech. 2012:135-164. DOI: 10.5772/53490
- [3] Whittingham MS. Lithium batteries and cathode materials. *Chemical Reviews*. 2004;**104**:4271-4301. DOI: 10.1021/cr020731c
- [4] Lu L, Han X, Li J, Hua J, Ouyang M. A review on the key issues for lithium-ion battery management in electric vehicles. *Journal of Power Sources*. 2013;**226**:272-288. DOI: 10.1016/j.jpowsour.2012.10.060
- [5] Conte FV. Battery and battery management for hybrid electric vehicles: A review. *e & i Elektrotechnik und Informationstechnik*. 2006;**123**:424-431. DOI: 10.1007/s00502-006-0383-6
- [6] Ritchie AG. Recent developments and future prospects for lithium rechargeable batteries. *Fuel and Energy Abstracts*. 2002;**43**:193. DOI: 10.1016/s0140-6701(02)85787-3
- [7] Lv D, Shao Y, Lozano T, Bennett WD, Graff GL, Polzin B, et al. Failure mechanism for fast-charged lithium metal batteries with liquid electrolytes. *Advanced Energy Materials*. 2015;**5**:1-7. DOI: 10.1002/aenm.201400993
- [8] Xu W, Wang J, Ding F, Chen X, Nasybulin E, Zhang Y, et al. Lithium metal anodes for rechargeable batteries. *Energy and Environmental Science*. 2014;**7**:513-537. DOI: 10.1039/c3ee40795k
- [9] Ould Ely T, Kamzabek D, Chakraborty D. Batteries safety: Recent progress and current challenges. *Frontiers in Energy Research*. 2019;**7**:1-44. DOI: 10.3389/fenrg.2019.00071
- [10] Liu Z, Huang Y, Huang Y, Yang Q, Li X, Huang Z, et al. Voltage issue of aqueous rechargeable metal-ion batteries. *Chemical Society Reviews*. 2020;**49**:180-232. DOI: 10.1039/c9cs00131j
- [11] Wang Y, Zhong WH. Development of electrolytes towards achieving safe and high-performance energy-storage devices: A review. *ChemElectroChem*. 2015;**2**:22-36. DOI: 10.1002/celec.201402277
- [12] Srivastava S, Schaefer JL, Yang Z, Tu Z, Archer LA. 25th anniversary article: Polymer-particle composites: Phase stability and applications in electrochemical energy storage. *Advanced Materials*. 2014;**26**:201-234. DOI: 10.1002/adma.201303070
- [13] Aziz SB. Li⁺ ion conduction mechanism in poly (ϵ -caprolactone)-based polymer electrolyte. *Iranian Polymer Journal (English Edition)*. 2013;**22**:877-883. DOI: 10.1007/s13726-013-0186-7
- [14] Wright P v. Electrical conductivity in ionic complexes of poly(ethylene oxide). *British Polymer Journal*. 1975;**7**:319-327. DOI: 10.1002/pi.4980070505
- [15] Armand M. Polymer electrolytes. *Annual Review of Materials Science*. 1986;**16**:245-261. DOI: 10.1002/9783527611676.ch20
- [16] Cheng S, Smith DM, Li CY. How does nanoscale crystalline structure affect ion transport in solid polymer electrolytes? *Macromolecules*. 2014;**47**:3978-3986. DOI: 10.1021/ma500734q

- [17] Johansson P. First principles modelling of amorphous polymer electrolytes: Li⁺-PEO, Li⁺-PEI, and Li⁺-PES complexes. *Polymer*. 2001;**42**:4367-4373. DOI: 10.1016/S0032-3861(00)00731-X
- [18] Geiculescu OE, Hallac BB, Rajagopal RV, Creager SE, Desmarteau DD, Borodin O, et al. The effect of low-molecular-weight poly(ethylene glycol) (PEG) plasticizers on the transport properties of lithium fluorosulfonimide ionic melt electrolytes. *Journal of Physical Chemistry B*. 2014;**118**:5135-5143. DOI: 10.1021/jp500826c
- [19] Song JY, Wang YY, Wan CC. Review of gel-type polymer electrolytes for lithium-ion batteries. *Journal of Power Sources*. 1999;**77**:183-197. DOI: 10.1016/S0378-7753(98)00193-1
- [20] Manuel Stephan A, Nahm KS. Review on composite polymer electrolytes for lithium batteries. *Polymer*. 2006;**47**:5952-5964. DOI: 10.1016/j.polymer.2006.05.069
- [21] Xue Z, He D, Xie X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. *Journal of Materials Chemistry A*. 2015;**3**:19218-19253. DOI: 10.1039/c5ta03471j
- [22] Long L, Wang S, Xiao M, Meng Y. Polymer electrolytes for lithium polymer batteries. *Journal of Materials Chemistry A*. 2016;**4**:10038-10039. DOI: 10.1039/c6ta02621d
- [23] Chen R, Qu W, Guo X, Li L, Wu F. The pursuit of solid-state electrolytes for lithium batteries: From comprehensive insight to emerging horizons. *Materials Horizons*. 2016;**3**:487-516. DOI: 10.1039/C6MH00218H
- [24] Edman L, Doeff MM, Ferry A, Kerr J, de Jonghe LC. Transport properties of the solid polymer electrolyte system P(EO)_nLiTFSI. *Journal of Physical Chemistry B*. 2000;**104**:3476-3480. DOI: 10.1021/jp993897z
- [25] Rivas BL, Maureira AE, Mondaca MA. Aminodiacetic water-soluble polymer-metal ion interactions. *European Polymer Journal*. 2008;**44**:2330-2338. DOI: 10.1016/j.eurpolymj.2008.05.001
- [26] Stephan AM, Kumar TP, Kulandainathan MA, Lakshmi NA. Chitin-incorporated poly(ethylene oxide)-based nanocomposite electrolytes for lithium batteries. *Journal of Physical Chemistry B*. 2009;**113**:1963-1971. DOI: 10.1021/jp808640j
- [27] Honary S, Orafi H. The effect of different plasticizer molecular weights and concentrations on mechanical and thermomechanical properties of free films. *Drug Development and Industrial Pharmacy*. 2002;**28**:711-715. DOI: 10.1081/DDC-120003863
- [28] Mohapatra SR, Thakur AK, Choudhary RNP. Effect of nanoscopic confinement on improvement in ion conduction and stability properties of an intercalated polymer nanocomposite electrolyte for energy storage applications. *Journal of Power Sources*. 2009;**191**:601-613. DOI: 10.1016/j.jpowsour.2009.01.100
- [29] Mulmi S, Park CH, Kim HK, Lee CH, Park HB, Lee YM. Surfactant-assisted polymer electrolyte nanocomposite membranes for fuel cells. *Journal of Membrane Science*. 2009;**344**:288-296. DOI: 10.1016/j.memsci.2009.08.028
- [30] Agrawal RC, Pandey GP. Solid polymer electrolytes: Materials designing and all-solid-state battery applications: An overview. *Journal of Physics D: Applied Physics*. 2008;**41**:223001(1-18). DOI: 10.1088/0022-3727/41/22/223001

- [31] Lu J, Yan F, Texter J. Advanced applications of ionic liquids in polymer science. *Progress in Polymer Science* (Oxford). 2009;**34**:431-448. DOI: 10.1016/j.progpolymsci.2008.12.001
- [32] Amde M, Liu JF, Pang L. Environmental application, fate, effects, and concerns of ionic liquids: A review. *Environmental Science and Technology*. 2015;**49**:12611-12627. DOI: 10.1021/acs.est.5b03123
- [33] Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry*. 2001;**3**:156-164. DOI: 10.1039/b103275p
- [34] Zhang S, Sun N, He X, Lu X, Zhang X. Physical properties of ionic liquids: Database and evaluation. *Journal of Physical and Chemical Reference Data*. 2006;**35**:1475-1517. DOI: 10.1063/1.2204959
- [35] Abitelli E, Ferrari S, Quartarone E, Mustarelli P, Magistris A, Fagnoni M, et al. Polyethylene oxide electrolyte membranes with pyrrolidinium-based ionic liquids. *Electrochimica Acta*. 2010;**55**:5478-5484. DOI: 10.1016/j.electacta.2010.04.099
- [36] Balo L, Gupta H, Singh SK, Singh VK, Kataria S, Singh RK. Performance of EMIMFSI ionic liquid based gel polymer electrolyte in rechargeable lithium metal batteries. *Journal of Industrial and Engineering Chemistry*. 2018;**65**:137-145. DOI: 10.1016/j.jiec.2018.04.022
- [37] de Vries H, Jeong S, Passerini S. Ternary polymer electrolytes incorporating pyrrolidinium-imide ionic liquids. *RSC Advances*. 2015;**5**:13598-13606. DOI: 10.1039/c4ra16070c
- [38] Shalu BL, Gupta H, Singh VK, Singh RK. Mixed anion effect on the ionic transport behavior, complexation and various physicochemical properties of ionic liquid based polymer gel electrolyte membranes. *RSC Advances*. 2016;**6**:73028-73039. DOI: 10.1039/c6ra10340e
- [39] Nakagawa H, Izuchi S, Kuwana K, Nukuda T, Aihara Y. Liquid and polymer gel electrolytes for lithium batteries composed of room-temperature molten salt doped by lithium salt. *Journal of the Electrochemical Society*. 2003;**150**:A695. DOI: 10.1149/1.1568939
- [40] Pappenfus TM, Henderson WA, Owens BB, Mann KR, Smyrl WH. Complexes of lithium imide salts with tetraglyme and their polyelectrolyte composite materials. *Journal of the Electrochemical Society*. 2004;**151**:A209. DOI: 10.1149/1.1635384
- [41] Wu L. Chloride ion conducting polymer electrolytes based on cross-linked PMMA-PP14Cl-PP14TFSI ion gels for chloride ion batteries. *International Journal of Electrochemical Science*. 2019;**14**:2414-2421. DOI: 10.20964/2019.03.49
- [42] Balo L, Shalu GH, Kumar Singh V, Kumar Singh R. Flexible gel polymer electrolyte based on ionic liquid EMIMTFSI for rechargeable battery application. *Electrochimica Acta*. 2017;**230**:123-131. DOI: 10.1016/j.electacta.2017.01.177
- [43] Shin JH, Henderson WA, Passerini S. Ionic liquids to the rescue? Overcoming the ionic conductivity limitations of polymer electrolytes. *Electrochemistry Communications*. 2003;**5**:1016-1020. DOI: 10.1016/j.elecom.2003.09.017
- [44] Singh VK, Shalu CSK, Singh RK. Development of ionic liquid mediated novel polymer electrolyte membranes for application in Na-ion batteries. *RSC*

Advances. 2016;**6**:40199-40210. DOI: 10.1039/c6ra06047a

[45] Singh VK, Singh SK, Gupta H, Shalu BL, Tripathi AK, et al. Electrochemical investigations of $\text{Na}_{0.7}\text{CoO}_2$ cathode with PEO-NaTFSI-BMIMTFSI electrolyte as promising material for Na-rechargeable battery. *Journal of Solid State Electrochemistry*. 2018;**2**:1-11. DOI: 10.1007/s10008-018-3891-5

[46] Rupp B, Schmuck M, Balducci A, Winter M, Kern W. Polymer electrolyte for lithium batteries based on photochemically crosslinked poly(ethylene oxide) and ionic liquid. *European Polymer Journal*. 2008;**44**:2986-2990. DOI: 10.1016/j.eurpolymj.2008.06.022

[47] Gupta H, Shalu BL, Singh VK, Chaurasia SK, Singh RK. Effect of phosphonium based ionic liquid on structural, electrochemical and thermal behaviour of polymer poly(ethylene oxide) containing salt lithium bis(trifluoromethylsulfonyl)imide. *RSC Advances*. 2016;**6**:87878-87887. DOI: 10.1039/c6ra20393k

[48] Singh VK, Shalu BL, Gupta H, Singh SK, Singh RK. Solid polymer electrolytes based on Li^+ /ionic liquid for lithium secondary batteries. *Journal of Solid State Electrochemistry*. 2017;**21**:1713-1723. DOI: 10.1007/s10008-017-3529-z

[49] Gupta H, Kataria S, Balo L, Singh VK, Singh SK, Tripathi AK, et al. Electrochemical study of ionic liquid based polymer electrolyte with graphene oxide coated LiFePO_4 cathode for Li battery. *Solid State Ionics*. 2018;**320**:186-192. DOI: 10.1016/j.ssi.2018.03.008

[50] Balo L, Gupta H, Singh SK, Singh VK, Tripathi AK, Srivastava N, et al. Development of gel polymer electrolyte based on LiTFSI and

EMIMFSI for application in rechargeable lithium metal battery with GO-LFP and NCA cathodes. *Journal of Solid State Electrochemistry*. 2019;**23**:2507-2518. DOI: 10.1007/s10008-019-04321-6

[51] Gupta H, Shalu BL, Singh VK, Singh SK, Tripathi AK, et al. Effect of temperature on electrochemical performance of ionic liquid based polymer electrolyte with $\text{Li}/\text{LiFePO}_4$ electrodes. *Solid State Ionics*. 2017;**309**:192-199. DOI: 10.1016/j.ssi.2017.07.019

[52] Gupta H, Singh SK, Singh VK, Tripathi AK, Srivastava N, Tiwari RK, et al. Development of polymer electrolyte and cathode material for Li-batteries. *Journal of the Electrochemical Society*. 2019;**166**:A5187-A5192. DOI: 10.1149/2.0331903jes

[53] Wang C, Yang Y, Liu X, Zhong H, Xu H, Xu Z, et al. Suppression of lithium dendrite formation by using LAGP-PEO (LiTFSI) composite solid electrolyte and lithium metal anode modified by PEO (LiTFSI) in all-solid-state lithium batteries. *ACS Applied Materials and Interfaces*. 2017;**9**:13694-13702. DOI: 10.1021/acsami.7b00336

[54] An Y, Cheng X, Zuo P, Liao L, Yin G. Improved properties of polymer electrolyte by ionic liquid PP1.3TFSI for secondary lithium ion battery. *Journal of Solid State Electrochemistry*. 2012;**16**:383-389. DOI: 10.1007/s10008-011-1340-9

[55] Wetjen M, Kim GT, Joost M, Appetecchi GB, Winter M, Passerini S. Thermal and electrochemical properties of PEO-LiTFSI-Pyr 14TFSI-based composite cathodes, incorporating 4V-class cathode active materials. *Journal of Power Sources*. 2014;**246**:846-857. DOI: 10.1016/j.jpowsour.2013.08.037

[56] Zhu C, Cheng H, Yang Y. Electrochemical characterization of two

types of PEO-based polymer electrolytes with room-temperature ionic liquids. *Journal of the Electrochemical Society*. 2008;**155**:A569. DOI: 10.1149/1.2931523

[57] An Y, Cheng X, Zuo P, Liao L, Yin G. The effects of functional ionic liquid on properties of solid polymer electrolyte. *Materials Chemistry and Physics*. 2011;**128**:250-255. DOI: 10.1016/j.matchemphys.2011.03.007

[58] Kim GT, Appetecchi GB, Carewska M, Joost M, Balducci A, Winter M, et al. UV cross-linked, lithium-conducting ternary polymer electrolytes containing ionic liquids. *Journal of Power Sources*. 2010;**195**:6130-6137. DOI: 10.1016/j.jpowsour.2009.10.079

[59] Appetecchi GB, Kim GT, Montanino M, Alessandrini F, Passerini S. Room temperature lithium polymer batteries based on ionic liquids. *Journal of Power Sources*. 2011;**196**:6703-6709. DOI: 10.1016/j.jpowsour.2010.11.070