Enhancement of Li$^+$ ion conductivity in solid polymer electrolytes using surface tailored porous silica nanofillers

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Abstract
The current study represents the design and synthesis of polyethylene oxide (PEO)-based solid polymer electrolytes by solvent casting approach using surface tailored porous silica as nanofillers. The surface tailoring of porous silica nanostructure is achieved through silanization chemistry using 3-glycidyloxypropyl trimethoxysilane in which silane part get anchored to the silica surface whereas epoxy group get stellated from the silica surface. Surface tailoring of silica with epoxy group increases the room temperature electrochemical performances of the resulting polymer electrolytes. Ammonical hydrolysis of organosilicate precursor is used for both silica preparation and their surface tailoring. The composite solid polymer electrolyte films are prepared by solution mixing of PEO with lithium salt in presence of silica nanofillers and cast into film by solvent drying, which are then characterized by impedance measurement for conductivity study and wide angle x-ray diffraction for change in polymer crystallinity. Room temperature impedance measurement reveals Li$^+$ ion conductivity in the order of $10^{-4}$ S cm$^{-1}$, which is correlated to the decrease in PEO crystallinity. The enhancement of conductivity is further observed to be dependent on the amount of silica as well as on their surface characteristics.

Keywords: nanocomposites, polymer electrolytes, polymer crystallinity, ionic conductivity, Li$^+$ ion battery
Classification numbers: 5.11

1. Introduction
Realization of an efficient energy storage system, which can be used as an alternative source of continuous power supply for effective functioning of various electronic equipments, is the first step towards the development of a modern rechargeable battery. In this respect, Li$^+$ ion batteries are mostly favored as efficient energy storage systems in consumer electronics as well as other portable devices, which relies on their higher charge discharge capacity, longer cyclability, reliability and above all most economical. Growing demand of energy for emerging technologies used in consumer electronics, medical devices, electric vehicles, power tools etc, induces research interests for the development of novel electro-active materials to be used in Li$^+$ ion batteries for enhancing their room temperature ionic conductivity. Normally, the component in a Li$^+$ ion battery, which makes an interface between the two electrodes, is known as the electrolyte. Traditionally, liquid electrolytes are most commonly used in a Li$^+$ ion battery owing to their efficient ion transport capability across the two electrodes. But limitations associated with liquid electrolytes viz., problem in storage and transportation, leakage at electrode--
electrolyte interfaces, difficulty in handling and processing pave the way for development of a better alternative [1–3]. In this regard, solid polymer electrolytes are superior to its liquid counterparts in various aspects viz., stability, enhanced electrode–electrolyte compatibility, leakage proof, flexibility [4–6]. Although, polymer electrolytes have better characteristics than liquid electrolytes, the limitation of low ionic conductivity depletes its applicability as an efficient electrolyte for Li$^+$ ion batteries. Thus, intensive research is underway all over the world for the development of a suitable material to be used as a solid polymer electrolyte with unusual electro-chemical properties.

Mostly, polyethylene oxide (PEO) is used as the host polymer for constructing solid polymer electrolytes due to its better solubilising power for alkali metal salts, low $T_g$, high polarity and chemical stability. In fact, PEO in its amorphous state is a good ionic conductor, but the crystalline nature of PEO impedes its use as a host for solid polymer electrolytes. Various attempts have already been put forth for the enhancement of ionic conductivity of polymer electrolytes such as using liquid plasticizers, nano-inorganic oxides as fillers, polymer blending etc [1, 2, 7–9]. However, incorporating nanomaterials made of inorganic oxides as fillers in the polymer electrolytes, commonly known as nanocomposite polymer electrolytes (NCPE), are observed to be the most efficient not only because they helps in enhancement of ionic conductivity but also providing mechanical and thermal stability to the resulting polymer electrolytes [4, 5, 10, 11]. Thus, the combination of appropriate surface chemistry and nanoscience may eventually helps in augmenting the ionic conductivity of solid polymer electrolytes to a reasonable extent by altering the PEO crystallinity as well as by inducing novel properties.

Attempts have already been made to enhance the ionic conductivity of polymer electrolytes by incorporating silica as the inorganic fillers, but the result is not significant [12–15]. Further, it has been observed that end group of polymer matrix has an important role in modulating the conducting properties of PEO-silica-based NCPE due to their specific chemical interaction [16]. Grafting the surface of silica nanoparticles with a suitable polymer and utilize them as a filler in the formation of NCPE is also an effective way for enhancing the ionic conductivity of PEO based solid electrolytes. Liu et al used a composite nanoparticles in which fumed silica was grafted by co-polymerization of the poly (ethylene oxide) methacrylate with sodium 4-styrenesulfonate and observed an enhancement of conductivity, but up to $\sim 10^{-6}$ S cm$^{-1}$ only [17]. Nan et al [18] prepared PEO-based composite polymer electrolytes using SiO$_2$ filler modified with a silane coupling agent (KH550) and observed the ionic conductivity in the order of $\sim 10^{-6}$ S cm$^{-1}$. Lee et al [19] used SiO$_2$ nanoparticle grafted with short PEG chains with varying molecular weights for the construction of PEO-based composite electrolytes and observed an enhancement of ionic conductivity up to the order of $\sim 10^{-5}$ S cm$^{-1}$. Giannelis et al [20] incorporated a hyperbranched poly (amine-ester) grafted nano-silica into PVA-based composite electrolytes and observed an ionic conductivity in the order of $\sim 10^{-4}$ S cm$^{-1}$. Yap et al [21] demonstrated a size dependent ionic conductivity in PEO-based composite electrolytes in which nanosize silica show lower conductivity compared to their micron-size counterpart and maximum value obtained was in the order of $\sim 10^{-3}$ S cm$^{-1}$. Abdollahi et al [22] found that the presence of sulfonated polymer brushes onto the fumed silica nanoparticles enhances proton conductivity of the polymer electrolyte membranes. Agrawal et al [23] tethered the surface of silica nanoparticles with polyethylene glycol methyl ether (PEG) to form hairy nanoparticles which was applied for NCPE formation in presence of propylene carbonate. The enhancement of lithium ion conductivity due to modified silica filler can be attributed to the good dispersion in polymer electrolytes as well as to improved compatibility between the silica and polymer. Enhancement of ionic conductivity in PEO-based composite electrolytes using porous silica has also been reported, but the conductivity is far below for its practical application [10, 24–26].

Thus the basic idea generated from this literature review is to acknowledge the conducting properties of PEO through the use of properly functionalized porous silica nanostructure as the inorganic filler. In our previous work we have shown that use of porous silica nanostructure exhibit enhancement in ionic conductivity, which further depends on the amount of filler content in the polymer electrolytes [10]. Moreover, polymer to salt ratio also has a major contribution towards the variation of ionic conductivity. Shen et al [27] used a silane modified mesoporous silica SBA-15 to prepare PEO-based composite electrolytes, in which the entanglements between PEO chains and 3-glycidoxypropyl trimethoxysilane (3-GPTS) fragments attached to the surface of silica along with Lewis acid–base interactions were found to be responsible for the enhancement of Li$^+$ ion conductivity. Although higher lithium ion conductivity ($\sim 10^{-2}$ S cm$^{-1}$) is recorded above the melting temperature of PEO, the observed room temperature conductivity value still below $10^{-4}$ S cm$^{-1}$. Apart from nano-silica as fillers many modified oxide and their hybrid materials are also exploited as additives in the formation of NCPE, but still far away from the target value [21, 28–31]. As a consequence, there remains the possibility to modify the process in developing a novel NCPE, which can give lithium ion conductivity to reasonable higher values.

The present work is an extension of our previous study on effect of porous silica nano-filler on ionic conductivity of PEO-based NCPE [10]. Here, we report further enhancement in lithium ion conductivity of PEO by incorporating 3-GPTS functionalized porous silica nanostructure.

2. Experimental

2.1. Materials

Cetyltrimethylammonium bromide (CTAB), ammonium hydroxide solution (30%), sodium hydroxide (NaOH), tetraethyloxycholocate (TEOS), 3-glycidoxypropyl-trimethoxysilane (3-GPTS), PEO (Mw = 1000 000) and lithium trifluoromethanesulphonate (CF$_3$SO$_3$Li) were purchased from...
Alfa Aesar. All the chemicals were used as received without any further purification. PEO and lithium trifluoromethanesulphonate were dried in a vacuum oven at 50 °C for 24 h prior to their use. Double distilled water was used whenever required and dry acetonitrile was used as a solvent during the preparation of polymer electrolytes.

2.2. Synthesis of silica nanostructures (CTAB–SiO₂)

The preparation of porous silica nanostructures using the modified Stöber process is based on our earlier work [10]. First, a 0.1 M aqueous solution of CTAB was prepared in a round bottomed flask fitted with a tight stopper to which added the calculated amount of ammonium hydroxide solution. The mixture was magnetically stirred for 5 min followed by careful addition of TEOS to it. The mole ratio between various reactants during the experiment was maintained as follows, H₂O:NH₄OH:TEOS = 1:0.054:0.037. After 24 h of reaction at room temperature, the reaction mixture was centrifuged and washed with distilled water till the pH of the medium became neutral and finally three more times with alcohol. The resulting solid product was then vacuum dried at 70 °C for 48 h to get a white powder of silica nanostructures.

2.3. Synthesis of porous silica nanostructures by calcination (calcine-SiO₂)

The first method involves calcinations of the above silica nanostructure to burn out the organic part leaving behind the porous silica nanostructure. Thus, entrapped CTAB was removed from the silica nanostructures matrix by calcination of the as prepared silica nanostructures at 550 °C for 5 h, as reported in our earlier work [10].

2.4. Synthesis of porous silica nanostructures by chemical leaching (chem-SiO₂)

The second method involves chemical treatment instead of calcination to leach away the entrapped CTAB of the as-prepared silica nanostructures to get porous silica nanostructures. In brief, the excess CTAB present on the surface was removed by dispersing the above as prepared silica nanoparticles in a mixture of methanol–glacial acetic acid (95.5, v/v) and the solution was allowed to react as such for 15 h. After that the reaction mixture was centrifuged three times with double distilled water and one time with ethanol and then it was dried in vacuum at 60 °C for 48 h to get porous silica nanostructures devoid of CTAB.

2.5. Synthesis of epoxy coated porous silica nanostructures (epoxy-SiO₂)

Epoxy coated porous silica nanostructures were prepared using the same silane chemistry usually used in Stöber synthesis in which a precursor organometallic ligand (3-glycidoxypropyl-trimethoxysilane, 3-GPTS) was used containing the alkoxy silane group in one end for coupling to the silica surface and an epoxy group on the other end for functionalization. In a typical functionalization experiment, about 200 mg of porous silica nanostructures (obtained by calcinations) was dispersed in 100 ml of water in an air tight conical flask by ultrasonication. The pH of the dispersion was then adjusted to 10.5 using a few drops of 0.1 M NaOH. This was followed by the addition of 50 μl 3-GPTS with gentle magnetic stirring and was continued for another three days. The epoxy functionalized porous silica thus formed were purified by three cycles of centrifugation-washing with double distilled water and finally with ethanol. The solid product thus obtained was dried in vacuum at 60 °C for 48 h yielding a white powder of epoxy coated porous silica nanostructures (denoted as epoxy-SiO₂).

2.6. Synthesis of NCPE

The usual solvent casting approach was adopted for the synthesis of NCPE. Firstly, required amount of PEO and CF₃SO₃Li were solubilised in dry acetonitrile with a mole ratio of 15:1 by constant magnetic stirring. Sufficient time (6 h) was allowed for complete homogenization of the reaction mixture. Then required weight percent (i.e., 1%, 3%, 5% and 10% of total PEO-Li complex) of synthesized calcine-SiO₂ or chem-SiO₂ or epoxy-SiO₂ were dispersed in dry acetonitrile by ultrasonication and were added to the PEO-CF₃SO₃Li solution. The whole reaction mixture was kept on stirring overnight for complete mixing, which resulted in a transparent homogeneous mixture. The resulting reaction mixture was then poured in Teflon petri dishes and allowed to dry in room temperature for one day. This was further dried in a vacuum oven at 60 °C for one day to get a completely dry free standing polymeric NCPE film and stored in desiccators for further use.

2.7. Characterization

Microscopic analysis of silica nanostructures were performed using a FEI Tecnai G220 transmission electron microscope operating at 200 kV. The samples for analysis were prepared by making a thin film of silica nanostructures on a carbon coated copper grid by drop casting the corresponding ethanolic dispersion. Fourier transform infrared (FTIR) spectra were taken from the KBr pellet of the dry powder samples using a Bruker Alpha spectrometer. All measurements were conducted at ambient temperature with a resolution of 4 cm⁻¹. To monitor the change in polymer crystallinity in terms of change in the full width half maximum (FWHM) values of the polymer in different NCPEs, x-ray diffraction (XRD) measurements were carried out by D8 Advance, Bruker spectrometer using Cu Kα radiation source with wavelength 1.54 Å. For impedance measurement a part of the NCPE film was sliced into a small circular form and was placed between two disk type stainless steel electrodes, which was then placed into a customized sample holder connected to the PSM 1730 impedance analyzer and all measurements were performed at room temperature in the frequency range of 1 Hz–1 MHz. The data thus generated were then plotted in a Nyquist plot in which the intersection of the semicircle with the real axis gives the bulk resistance (R₀) of that particular
The modified stöber method was adopted to obtain silica nanostructures by ammonical hydrolysis of the organosilicate precursor i.e., TEOS in presence of CTAB template as reported in our earlier work [10]. The hydrolysis reaction was followed with the appearance of a milky colloidal suspension from a colorless solution indicating the formation of nanostructured silica on the CTAB template. The entrapped CTAB within the silica matrix was removed by using two approaches to obtain a porous silica nanostructure. Firstly, CTAB was removed thermally by calcinations of the resulting hybrid at 550 °C for 5 h as reported in our earlier work [10]. Secondly, CTAB was removed through chemical etching, i.e., by treatment with a dilute methanolic solution of acetic acid of the resulting hybrids. Adoption of a chemical etching process to remove CTAB from silica surface minimizes the loss of surface silanol groups and is advantageous over calcination, which endorses condensation of unreacted silanol groups and/or many surface functional groups [32]. Also, thermal treatment to remove CTAB may result in shrinkage of the nanopores in the silica nanostructure as well as alteration of the surface hydroxyl groups. Further, porous silica obtained by calcinations was functionalized with an epoxy silane (3-GPTS) in which the silane part got anchored to the silica surface through hydrolysis-coupling and the epoxy part got stellated away from the surface to be available for interaction with the PEO polymer matrix in the NCPE systems. A hypothetical schematic representation of 3-GPTS systems and after its functionalization on the silica surface is shown in figure 1.

Figure 2(A) shows the transmission electron microscopy (TEM) image of the silica nanostructures (chem-SiO2), in which CTAB is removed chemically by etching with dilute acid solution whereas figure 2(B) shows the silica nanostructure (epoxy-SiO2), in which CTAB is removed by calcination followed by epoxy coating using 3-GPTS. A close observation of the TEM images reveals that the nanostructures show similar morphology having pore structure. The above morphology can also be comparable to silica nanostructure (calcine-SiO2, in which CTAB is removed by calcination at 550 °C) reported in our earlier report indicating that surface of the nanostructure remains same in terms of their morphology, but may differ in surface functionality [10]. The porous nature of the materials as revealed in their respective TEM images has also been confirmed from low angle XRD measurement of calcine-SiO2 sample (low angle XRD is not shown here) [10]. The removal of CTAB and presence of epoxy group on the silica surface is confirmed from FTIR spectroscopy by observing the diminishing of the characteristic bands due to the CTAB molecules and is discussed in the subsequent section.

Figure 3 shows the FTIR studies for the dry powder samples of various silica nanostructures entrapped in KBr pellet. The spectrum for SiO2–CTAB sample shows the presence of signature band for CTAB molecule indicating its incorporation in the nanostructure. The bands at 2923 cm⁻¹ and 2853 cm⁻¹ respectively corresponds to asymmetric and symmetric stretching −CH2 of CTAB molecules, whereas the band due to −CH3 anti-symmetric deformation appears at 1477 cm⁻¹. The −CH2 torsional and −CH2−out/in-planes swinging bands are overlapped with the dominant Si−O−Si vibration appear at 1300−700 cm⁻¹. The presence of the tertiary amine is indicated by the presence of a weak broad band at 2500 cm⁻¹. The presence of the above mentioned bands corresponds well with that of free CTAB molecules and thus confirming its presence inside the SiO2 matrix. In comparison to silica in which CTAB is removed either by calcinations or by chemical etching, the signature bands for CTAB are not appeared. Even if it is present, e.g., the bands due to −CH2 asymmetric and symmetric stretching at 2923 cm⁻¹ and 2853 cm⁻¹ respectively, is relatively very weak with respect to the silica bands and can be assumed negligible for any surface studies. The 3-GPTS (epoxy) functionalization on silica surface was confirmed by the appearance of strong bands at 2927 cm⁻¹ and 2856 cm⁻¹ respectively corresponds to asymmetric and symmetric stretching −CH2 group. All other bands are overlapped with the dominating Si−O−Si band and thus are not distinguishable. The above result elucidated the epoxy capping on the surface of calcined porous silica nanostructure. Further, the appearance of a broad band at ~3450 cm⁻¹ due to the surface −OH groups in CTAB–SiO2 and epoxy-SiO2 confirms their successful immobilization on silica surface.
To study the impact of our noble nano fillers towards the conductivity of PEO-CF$_3$SO$_3$Li polymer electrolytes, AC impedance measurements were carried out using a customized sample holder, in which the NCPE films were sandwiched between two stainless steel disk electrodes. AC impedance measurements were carried out at a frequency range of 1 Hz–1 MHz at a constant voltage. The data generated from the measurements were then plotted in Nyquist plots to determine lithium ion conductivity. The corresponding Nyquist plots for various NCPE films with different weight percentage of nano fillers are shown in figures 4 and 5. A standard Nyquist plot gives a complete semi-circle in the region of high frequency and an inclined/straight line in the low frequency portion but we observe an incomplete semi-circle and an inclined line which may be arises due to variation in different polymer films in terms of structure, surface roughness and thickness [33–35]. Further, to obtain the bulk resistance ($R_b$) values of the respective NCPE films, the resulting data points are fitted using the z-view software. Our previous studies on use of 1% calcine-SiO$_2$ nano filler without any surface modification shows the ionic conductivity $\sim 5.41 \times 10^{-6}$ S cm$^{-1}$, which decreases with the increase in filler contents as calculated from its corresponding $R_b$ values [10]. Under the similar instrumental setup the $R_b$ values estimated from the respective Nyquist plot of NCPE films prepared with chem-/epoxy-SiO$_2$ filler also shows an increasing trend with increase in the filler contents. Consequently, the NCPE films with 1% chem-/epoxy-SiO$_2$ filler shows the lowest $R_b$ values whereas the film with 10% filler contents shows the highest values. As a result, the lithium ion

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**Figure 2.** The TEM images of the porous silica nanostructures: (A) chem-SiO$_2$, CTAB is removed by chemical etching and (B) epoxy-SiO$_2$, CTAB is removed by calcinations followed by surface tailoring with 3-GPTS.

**Figure 3.** FTIR spectra of various silica nanostructures used as nano fillers in composite designing, in which the presence/absence of the $-\text{CH}_2$ vibration in the nano fillers indicating the presence/absence of the organic functionality.

**Figure 4.** Nyquist plot of the data obtained from AC impedance measurement of NCPE films prepared using chem-SiO$_2$ nano fillers. The plot gives the bulk resistance from which the Li$^+$ ion conductivity is calculated.
The plot gives the bulk resistance from which the Li$^+$ conductivity of various NCPE films prepared with chem-SiO$_2$ shows the conductivity of $4.20 \times 10^{-5}$ S cm$^{-1}$, $1.73 \times 10^{-5}$ S cm$^{-1}$, $1.35 \times 10^{-5}$ S cm$^{-1}$ and $8.08 \times 10^{-6}$ S cm$^{-1}$ for filler contents of 1%, 3%, 5% and 10%, respectively. Whereas the lithium ion conductivity of various NCPE films prepared with epoxy-SiO$_2$ shows the conductivity of $1.03 \times 10^{-4}$ S cm$^{-1}$, $3.02 \times 10^{-5}$ S cm$^{-1}$, $2.87 \times 10^{-5}$ S cm$^{-1}$ and $1.50 \times 10^{-5}$ S cm$^{-1}$ for filler contents of 1%, 3%, 5% and 10%, respectively.

Thus, PEO-CF$_3$SO$_3$Li NCPE with 1% nanofiller (calcine-/chem-/epoxy-SiO$_2$) displays highest room temperature conductivity which is in the order of $10^{-4}$ for epoxy-SiO$_2$ and $10^{-5}$ for chem-SiO$_2$, higher than our previous studies [10]. The conductivity values decreases subsequently with increase in the weight percent of chem-/epoxy-SiO$_2$ nanofillers as can also be seen from table 1. The results thus infers that the lithium ion conductivity of NCPE can be enhanced up to $\sim 20$ times simply by functionalization of the calcine-SiO$_2$ nanofiller with epoxy group using 3-GPTS in which the silane group is used for anchoring to the silica surface leaving behind the epoxy group stellated from the silica surface. The surface bound epoxy group on the silica surface can interact with the PEO matrix through non-covalent interaction thereby helps in better dispersibility of silica fillers within the matrix. The homogeneously dispersed silica thus prevents PEO crystallization and increases the amorphous nature of the polymer which may assist in enhancing the lithium conductivity of the resulting NCPE films. Further, decrease in ionic conductivity of NCPE films with increase of silica filler contents above 1% can be ascribed due to its insulating property, the presence of which inhibits the lithium ion mobility and thus causes a decrease of ionic conductivity. Hence, optimum amount of silica is necessary for enhancing the ionic conductivity of PEO based NCPE films. Zhao et al [17] has also reported identical observation by applying polyelectrolyte tuned silica nanoparticles as nanofiller for polymer electrolyte in which they observed enhancement of ionic conductivity using an optimum amount of nanofiller and above which conductivity decreased.

Figure 6 shows the wide angle XRD plots of various NCPE films prepared with epoxy-SiO$_2$ nanofillers. The plot shows the crystalline peaks for pristine PEO, which does not vanish even after NCPE formation. This indicates that PEO maintaining its crystalline nature even after NCPE formation using silica nanofillers. Thus the enhancement of lithium ion conductivity can be explained on the basis of relative decrease of PEO crystallinity in presence of silica nanofillers. And the change of crystallinity can be calculated from the change of FWHM values of a particular XRD peak, e.g., increase in the FWHM value indicates decrease in polymer crystallinity and vice versa. As can be seen from figure 5, the NCPE having 1% epoxy-SiO$_2$ shows highest conductivity in the order of $\sim 10^{-4}$ S cm$^{-1}$ and that of NCPE having 10% epoxy-SiO$_2$ shows lowest conductivity in the order of $\sim 10^{-5}$ S cm$^{-1}$. Consequently, the NCPE having 1% epoxy-SiO$_2$ shows highest value of FWHM whereas the NCPE having 10% epoxy-SiO$_2$ shows lowest value of FWHM. As a result, the PEO in presence of 1% epoxy-SiO$_2$ is comparatively less

| Fillers          | $\delta$ (S cm$^{-1}$) | FWHM at $2\theta = 19^\circ$ |
|------------------|------------------------|------------------------------|
| 1% chem-SiO$_2$  | $4.20 \times 10^{-5}$   | 0.21715                      |
| 3% chem-SiO$_2$  | $1.73 \times 10^{-5}$   | 0.17524                      |
| 5% chem-SiO$_2$  | $1.35 \times 10^{-5}$   | 0.11704                      |
| 10% chem-SiO$_2$ | $8.08 \times 10^{-6}$   | 0.07129                      |
| 1% epoxy-SiO$_2$ | $1.03 \times 10^{-4}$   | 0.17554                      |
| 3% epoxy-SiO$_2$ | $3.02 \times 10^{-5}$   | 0.11448                      |
| 5% epoxy-SiO$_2$ | $2.87 \times 10^{-5}$   | 0.10984                      |
| 10% epoxy-SiO$_2$| $1.50 \times 10^{-5}$   | 0.09661                      |
crystalline (i.e., more amorphous) compared to other compositions. Thus, increase in amorphous nature of PEO results in increase of the segmental motion of the polymeric chain thereby facilitating better lithium ion mobility and hence enhancement of the lithium ion conductivity.

The above result confirms that the enhancement of lithium ion conductivity is achieved up to the order of $10^{-4}$ S cm$^{-1}$ by surface tailoring of nanosilica fillers using 3-GPTS. The enhancement of lithium ionic conductivity of PEO based NCPEs films may be due to the better surface characteristics of epoxy-SiO$_2$ nanoparticles as well as their huge surface area arises from their porous nature. At the same time, well dispersed silica surface acts as cross-linking sites for the PEO segments (the basis for Lewis acid–base type interaction), thereby hindering the polymer reorganization into the crystalline form, which may create additional lithium ion conducting pathways on the surface of silica fillers resulting in the enhancement of conductivity [27]. Further, bulkiness of the triflate anions (CF$_3$SO$_3$)$^-$ acts as a plasticizer thereby hindering PEO crystallization and thus the contribution towards anionic conductivity can be considered as negligible. Overall, the enhancement of lithium conductivity in PEO based NCPE films studied here can not only be explained based on only parameter as discussed above, but can be considered as an additive effect of all possible parameters.

4. Conclusion

In summary the work represents the design and synthesis of PEO-based solid polymer electrolytes by solvent casting approach using surface tailored porous silica as nanofillers. Ammonical hydrolysis of organosilicate precursor has been used for both silica preparation and their surface tailoring. The surface tailoring of silica nanostructure is achieved by hydrolysis of 3-GPTS in ammonium medium, which is confirmed by FTIR study. The composite solid polymer electrolyte films are then prepared by solution mixing of PEO with Li$^+$ ions in presence of silica nanofillers and cast into film by solvent drying, which are then characterized by impedance spectroscopy and wide angle XRD measurement. The study reveals that surface tailoring of silica with epoxy group increases the electrochemical performances of the resulting polymer electrolytes and the room temperature Li$^+$ ion conductivity is observed in the order of $10^{-4}$ S cm$^{-1}$, which is much higher than the composites prepared with untailed silica nanostructures. The enhancement of conductivity is directly corroborated to the decrease in PEO crystallinity as observed from the change in FWHM values of XRD peaks. Moreover the enhancement of conductivity is further observed to be dependent on the amount of silica as well as on their surface characteristics, both of which can be explained on the basis of better dispersibility of the nanofillers in the polymer matrix of the resulting composites.

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