Fire Retardant, Superionic Solid State Polymer Electrolyte Membranes for Lithium Ion Batteries

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Abstract:

Recent advances on polymer electrolyte membranes (PEM) are reviewed with emphasis on fabrication and evaluation of electrochemical performance of solid PEMs consisted of photo-curable polymer precursor, lithium salt, and solid plasticizer. Guided by the phase diagram of ternary mixtures of poly(ethylene glycol) derivatives, lithium bis(trifluoromethane)sulfonyl imide (LiTFSI) salt, and succinonitrile (SCN) plasticizer, the achievement of completely amorphous, solid PEMs has been demonstrated. These solid PEM films are stretchable, thermally stable, and flame-retardant, showing enhanced high ionic conductivity on the level of superionic conductors. Electrochemical stability of the PEM has been tested in half-cell configurations using LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes against lithium foil counter electrode and their future prospects are discussed.

Review on liquid and gel electrolytes for lithium ion battery:

With rapid advancement of portable electronics and increasing demand for “green” electric vehicles (EV), rechargeable polymer lithium ion (Li^+) batteries have been the subject of immense interest. Due to rapid decline of fossil fuels and consequential pollution, scientists have been seeking ways of alleviating energy shortage and sustainable environment. To reduce the dependence on fossil fuels, higher energy storage systems such as lithium ion batteries have been immensely sought for EV and hybrid vehicles (HEV).

By virtue of reasonably high power and high energy density, liquid lithium ion battery has been the front runner of energy storage systems for EVs and aero-space applications. Over the years, the liquid Li^+ batteries have shown considerable improvement in safety and reliability in most low-power applications including smart phones, laptops, and wearable devices. However, the safety issue of battery combustion and fire remains a major obstacle in high-power battery applications in EVs or air-planes [1], which is attributable to flammable solvents utilized in these liquid electrolyte batteries [2].

Conventional liquid electrolytes in Li^+ batteries are basically solutions of a lithium salt dissolved in solvent mixtures such as ethylene carbonate (EC) or propylene carbonate (PC) with diethyl carbonate (DEC) [3] or dimethyl carbonate (DMC) [4,5]. EC, being highly polar (i.e., large dielectric permittivity) organic solvent, is capable of dissolving lithium ions efficiently from their salt, but it is a crystalline solid at ambient having a melting transition temperature of 38 °C. Hence, EC has been customarily mixed with low viscosity solvents (DEC, DMC) in order to prevent its crystallization and afford fast ion transport. Although the flash point (T_f) of EC is considerably high (i.e., 160 °C), but the flash points of co-solvents (DEC and DMC) are as low

as 31 °C and 18 °C, respectively [6]. Hence, these liquid electrolytes must be operated in robust plastic or metal containers. Even under normal operation conditions, heat can be accumulated inside the battery and raise temperature easily above the solvent evaporation temperature or the flash point, which in turn causes internal vapor pressure build-up [7]. Without proper casing and thermal management, volatile electrolyte solvents can leach out and eventually catch fire.

Over charging/discharging, internal short circuiting, or physical damage of container are additional factors that can compromise battery safety [7–10]. However, volatile solvents and their vapor pressure are still regarded as the major flammable cause of battery explosion. Therefore, in order to eliminate, or at least reduce the risk of the fire hazard of liquid electrolyte batteries, it is necessary to replace the traditional solvent electrolytes with safer electrolytes. One strategy is reducing the solvent amount by employing gel-type electrolytes [11], which are composed of polymeric networks soaked with solvent electrolytes. However, fire hazard could not be eliminated fully due to the potential volatility of solvents. Another straightforward idea is to replace the flammable solvents with solid, nonflammable materials such as solid electrolytes. In addition to their known flame-retardant property, many solid polymer electrolytes can form self-standing films, which can be mechanically sturdy and/or flexible [12]. Some of these solid polymer electrolyte mixtures can be processed into thin films from their melt state, which may be assembled to afford flexible solid Li^+ batteries for use in portable electronics and devices.

Generally, solid electrolytes include inorganic ceramic electrolytes and organic solid polymer electrolytes. Inorganic ceramic electrolytes can withstand high temperatures, owing to their inorganic nature, which have exhibited reasonably high ionic conductivity on the level of 10^{-4} S/cm to 10^{-2} S/cm [13–16]. Generally speaking, most inorganic electrolytes are rigid

crystalline powders and thus poor in melt-processability requiring high energy cost to fabricate and also suffer from poor interfacial compatibility with the electrodes. There are some works where inorganic electrolytes were incorporated in poly(ethylene oxide)/lithium salt mixture [17] or polyacrylonitrile/lithium salt mixture [18]. The room temperature ionic conductivity is on the level of 10^{-4} S/cm, which needs to be improved to reach the superionic conductor level of 10^{-3} S/cm for commercial realization. Alternatively, thermoplastic and/or thermosetting polymers have been sought for solid electrolytes in order to alleviate the flammable issues of organic solvents. Solid polymer electrolytes are more flexible, easy to process, and cost-effective as compared to inorganic ceramic electrolytes. However, the room temperature ionic conductivity of most solid polymer electrolytes remains low at 10^{-4} S/cm [19], which is far below the superionic conductor level. Hence, development of highly conductive PEMs has remained one of the major challenges to achieve the aforementioned goals.

Solid polymer electrolytes are attractive alternative, which eliminate most short comings of the liquid electrolytes such as corrosion of the electrode during charge/discharge cycling and/or short-circuiting due to the formation of dendritic crystals on the electrode surface. The early generation of polymer electrolytes is composed of lithium salts dissolved in poly(ethylene oxide) (PEO). However, the room temperature (RT) ionic conductivity of these PEO-based polymer electrolytes is rather poor (i.e., 10^{-9} ~ 10^{-6} S/cm) and thus hardly meet the requirement of the superionic conductor level.

Although PEO chain in the PEMs is capable of transporting ions through its rapid segmental mobility depending on its glass transition temperature (T_g) [20], molecular dynamics simulations [21] revealed that Li cations are transported through PEO medium that formed ion-dipole

complexation between Li^+ and ether oxygens. Hence, the overall Li ion conduction in PEO-based electrolytes relies on Li^+ motion through conformational ‘*trans-gauche*’ transformation of the PEO chains in a manner dependent on local segmental motion of the matrix. In general, there are two approaches to improve the ionic conductivity of polymer electrolytes: one is to synthesize new host polymers with low T_g and **the other is to reduce the T_g of existing host polymers by adding solid or non-volatile plasticizers**. No matter which approach is adopted, the crystallinity of PEO in those electrolytes should be eliminated or suppressed as much as possible.

To achieve higher ionic conductivity, siloxane units have been introduced into host polymers since it can lower the T_g of the host polymer. For instance, PEMs containing linear ethylene oxide - dimethylsiloxane copolymers having a very low T_g of -80°C showed reasonable room temperature ionic conductivity of 10^{-4} S/cm [22,23]. A comparable ionic conductivity was also demonstrated in PEMs containing comb-like branched polysiloxanes [24–26]. According to Walkowiak et al, who synthesized host polymer with siloxane backbone grafted with tris(2-methoxyethoxy)(vinyl)silane, the room temperature ionic conductivity has exceeded 10^{-4} S/cm [27].

In literature, the addition of small amount of ceramic fillers into PEO-based PEMs has been claimed to improve the ionic conductivity [28–30]. Croce et al. reported the ionic conductivity enhancement of PEO- LiClO_4 electrolytes upon incorporation of Al_2O_3 and TiO_2 [29], but the room temperature ionic conductivity of the starting PEO- LiClO_4 electrolytes without these metal oxide fillers was very poor, i.e., less than 10^{-8} S/cm. With the addition of 10 wt% of Al_2O_3 and TiO_2 fillers, the crystallinity of PEO was suppressed and consequently the room temperature

ionic conductivity had improved to the level of 10^{-5} S/cm; this improvement is still insufficient for practical purposes [29].

In gel-type electrolytes, the addition of liquid plasticizers can improve the ionic conductivity of PEM by efficiently suppressing the crystallization and/or lowering the T_g of the host polymers. One common type of liquid plasticizers that have been widely used in conventional liquid electrolytes is aprotic organic solvent, viz., EC [31–33] and PC [34,35]. On the other hand, oligomeric poly(ethylene glycols) and their derivatives [36–38], as well as phthalate derivatives [39] can also work as liquid plasticizers. Generally, the ionic conductivity of PEMs has been claimed to reach the level of 10^{-5} - 10^{-4} S/cm by simply plasticizing with liquid plasticizers [34]. However, reintroduction of liquid plasticizers to the PEM defeats the purpose of improving battery safety. Moreover, the concern on thermal stability of electrolytes containing liquid plasticizers was raised by Nicotera et al [40], who noticed the loss of organic liquid plasticizer due to evaporation during annealing in vacuum, resulting in the rapid decline of ionic conductivity. Even though the above condition does not represent the actual environment in battery operation, thermal stability of gel-type electrolytes should receive closer scrutiny, especially under vacuum.

Recent advances on polymer electrolyte membranes:

Plastic crystals may be categorized as a class of solid plasticizer. A typical example is succinonitrile (SCN), which exhibits a plastic crystal phase between its crystal melting temperature of -38°C and plastic crystal – isotropic melt transition at 58°C [41]. Long and co-workers were the first to demonstrate the fast ion conduction in molecular plastic crystals containing SCN plastic crystals and lithium salts [42]. However, these SCN/lithium salt mixtures

have paste-like appearance without mechanical sturdiness. Armand et al showed the role of the plastic-crystalline phase of SCN as a universal matrix for solid-state ionic conductors [43,44]. Subsequently, plastic crystalline SCN has been employed as solid plasticizer to the polymer electrolyte membrane (PEM) containing PEO/lithium salt composites, whereby PEO serves as the matrix [45,46].

Figure 1. (a) Ternary phase diagram of PEGDMA/SCN/LiTFSI at 25 °C. Wide isotropic region (white) suggests a potential processing composition window for completely amorphous PEMs. Region A represents LiTFSI crystal coexisted with liquid SCN and PEGDMA. Region B represents coexistence of plastic crystal SCN with amorphous PEGDMA and LiTFSI. (b) RT ionic conductivity of the fabricated PEMs in relation to the indicated compositions of the RT ternary phase diagram.

Recently, Echeverri et al successfully fabricated completely amorphous plasticized solid polymer electrolytes under the guidance of ternary mixtures of PEO/SCN/LiTFSI [41]. They demonstrated that room temperature ionic conductivity of some completely amorphous compositions can reach the superionic conductor level, i.e., as high as 2.9×10^{-3} S/cm at the 35/35/30 PEO/SCN/LiTFSI composition. Of particular interest is that amorphous SCN not only plasticizes the polymer matrix, but also can ionize the LiTFSI salt. Since PEO is the linear

polymer, the above completely amorphous PEMs, although formed self-standing films, are fragile (elongation at break of ~5%) with low mechanical strength and modulus. To improve the above short-comings, photo-crosslinking strategies have been adopted to fabricate various polymeric electrolyte membranes in order to afford strong mechanical support and flexibility to the PEM composites [47,48].

In this article, we presented two PEO-based precursors, poly(ethylene glycol) diacrylate (PEGDA) [47,48] and poly(ethylene glycol) dimethacrylate (PEGDMA) as polymeric networks by photo-polymerizing them in their SCN/LiTFSI mixtures. In Figure 1a, is shown the ternary phase diagram consisted of PEGDMA, SCN, and LiTFSI at 25 °C, exhibiting LiTFSI crystal + liquid, SCN plastic crystal + liquid, and wide isotropic liquid regions. Photo-polymerization was carried out at several compositions within the isotropic region to afford completely amorphous or partially crystalline/liquid crystalline PEMs. Most compositions in the isotropic region afforded completely amorphous PEM, but some compositions close to the coexistence envelopes of the plastic crystal + liquid or crystal + liquid coexistence regions, polymerization induced phase separation and crystallization can take place. Pictures A and B represent the optical micrographs of blends located at A and B, respectively. Polarized optical micrograph (POM) in region A exhibits highly birefringent crystalline entities, suggestive of the coexistence of LiTFSI crystal + liquid phase. However, the POM micrograph in the region B shows dark appearance due to the lack of orientation fluctuation, but the dendritic morphology can be seen clearly under the unpolarized condition, characteristics of the typical plastic crystalline phase of SCN associated with density fluctuation.

PEMs were fabricated via ultraviolet (UV) crosslinking of the ternary blends of

PEGDA/SCN/LiTFSI or PEGDMA/SCN/LiTFSI at various compositions. The PEMs were sandwiched between two stainless steel plates for ionic conductivity measurement. The ionic conductivity was measured by means of AC impedance measurement using the combination of Solatron 1287 electrochemical interface and 1260 impedance analyzer. Detailed experimental methods are described in reference [48].

Figure 2. (a) TGA thermogram of PEM (PEGDMA/SCN/LiTFSI 10/70/20) and (b-e) Flame test for PEM (PEGDA/SCN/LiTFSI 20/40/40) as a function of time, showing ignition at 5 s (c) and extinguishes in 2 s after moved away from the flame (d-e). Full video of this experiment may be viewed at <https://youtu.be/UiHe8coQU7o>

Figure 1b exhibits the RT ionic conductivities of the PEMs corresponding to the indicated compositions within the RT ternary phase diagram. The filled black bars representing the ionic conductivities along the composition line fixed at the PEGDMA/LiTFSI ratio of 1/2 as a function of SCN concentration. Within the isotropic amorphous region, the ionic conductivity of the PEMs increases with increasing SCN content to the maximum value of 3.2×10^{-3} S/cm at the 60% SCN, i.e., 13.3/60/26.7 PEGDMA/SCN/LiTFSI composition. Then it starts to decline as it enters the SCN plastic crystal region driven by polymerization-induced crystallization. On the other hand, the unfilled bar follows the composition line of PEGDMA content at the fixed ratio of

SCN/LiTFSI at 1/1. It is seen that the low PEGDMA concentration PEM composite shows reputable ionic conductivity of 1.6×10^{-3} S/cm at the 10/45/45 PEGDMA/SCN/LiTFSI composition, but it occurs at the expense of the poor mechanical support of the matrix. When the concentration of the matrix material (PEGDMA) is increased, the room temperature ionic conductivity value declines noticeably. Hence, it is desirable to optimize the PEM composite properties, i.e., the balance of high ionic conductivity and mechanical support of the matrix, for solid-state Li ion battery applications.

Figure 3. (a) Ionic conductivity variation of PEM 10/70/20 (PEGDMA/SCN/LiTFSI) and PEM 13.3/60/26.7 (PEGDMA/SCN/LiTFSI) with reciprocal absolute temperature; (b) PEM 10/70/20 (PEGDMA/SCN/LiTFSI) exhibiting stable ionic conductivity for 150mins at the isothermal temperatures of 60°C, 95°C, 115°C and 135°C.

Next, thermal stability of the PEM was investigated by means of TGA. In Figure 2a, are shown TGA thermograms of neat PEGDMA, LiTFSI, SCN and their PEM composite having the 10/70/20 (PEGDMA/SCN/LiTFSI) ratios. Both PEGDMA network and LiTFSI salt are thermally stable up to 330 and 370 °C, respectively. However, neat SCN, being a small molecule, is less stable undergoing thermal degradation in the vicinity of 115 °C. However, as manifested by the onset temperature of thermal degradation around 135 °C (i.e., the intersection point where

two tangent lines met), the 10/70/20 PEM (PEGDMA/SCN/LiTFSI) composition shows improved thermal stability. However, there appear dual drops in the PEM composite, which may be attributed to stabilization of SCN by PEGDMA and LiTFSI.

Figure 4. Cyclic voltammograms of (a) PEM (20/40/40 PEGDMA/SCN/LiTFSI) covering from -0.5V to 6.0V; (b) PEM (20/40/40 PEGDMA/SCN/LiTFSI) from -0.5V to 4.5V; (c) PEM (20/40/40 PEGDA/SCN/LiTFSI) from -0.5V to 6.0V; and (d) PEM (20/40/40 PEGDA/SCN/LiTFSI) from -0.5V to 4.5V. The scan rate was 1mV/s.

To better appreciate the flame retardant behavior of the solid PEM, A flame test was carried out for PEM (PEGDA/SCN/LiTFSI 20/40/40). Figure 2b shows that a strip of transparent PEM film was subjected to the flame test at 0 s. It takes about 5 s for the PEM film to catch fire (Figure 2c), suggesting slow ignition or flame retardant behavior. Interestingly, upon removal of

the PEM strip away from the flame, it extinguishes in 2 s (see Figures 2d and e), implying self-extinguishable character. Qualitatively, the above flame retardant test suggests that PEM (PEGDA/SCN/LiTFSI 20/40/40) may be not only flame retardant, but also self-extinguishable.

The ionic conductivity of two PEM compositions was subsequently measured as a function of temperature. The ionic conductivity of the 13.3/60/26.7 PEM (PEGDMA/SCN/LiTFSI) increases almost linearly with reciprocal absolute temperature up to 135 °C investigated (Figure 3a), suggestive of Arrhenius type. The apparent activation energy for ion transport is customarily calculated in accordance with Arrhenius equation or by Vogel-Tammann-Fulcher (VTF) equation. The Arrhenius plot seems to be adequate for the present case. The apparent activation energy thus obtained from the Arrhenius plot is about 17 ~ 20 kJ/mole. Echeverri et al [47] reported that the apparent activation energy decreased from 50 kJ/mol to about 28 kJ/mol with increasing SCN concentration from 5 wt.% to 50 wt.%. In the present work, the concentration of SCN was extended to 60 - 70wt.% wherein the apparent activation energy further decreased to about 17 ~ 20 kJ/mole. This implies that increasing SCN plasticizer concentration lowers the apparent activation energy barrier, thereby expediting the ion transport. It should be emphasized that the 10/70/20 PEM shows a change of slope at around 35 °C, which may be attributed to the plastic crystal melting transition of SCN in the PEM.

The stability of PEMs was further demonstrated by performing the isothermal measurement of ionic conductivity at various temperatures from 60 to 135 °C. As expected, the ionic conductivity value of the 10/70/20 PEM (PEGDMA/SCN/LiTFSI) increases with increasing temperatures and also remains stable at isothermal temperatures of 60 and 95 °C. However, there is a slight decrease (about 5%) in the conductivity values at isothermal annealing 115 and 135°C

for 150 mins tested (Figure 3b). Although the above PEMs possess outstanding ionic conduction capability and reasonable thermal stability, electrochemical stability should be further evaluated for battery applications.

Figure 5. (a) Variation of voltage as a function of specific capacity for LiFePO₄/PEM(20/40/40 PEGDA/SCN/LiTFSI)/Li half-cell and (b) voltage as a function of specific capacity for Li₄Ti₅O₁₂/PEM(20/40/40 PEGDA/SCN/LiTFSI)/Li half-cell. (c) Variation of specific capacity as a function of number of cycles for LiFePO₄/PEM(20/40/40 PEGDA/SCN/LiTFSI)/Li half-cell and (d) specific capacity as a function of number of cycles for Li₄Ti₅O₁₂/PEM(20/40/40 PEGDA/SCN/LiTFSI)/Li half-cell.

Next, PEM was assembled into coin cells with stainless steel as a working electrode and Li metal as a reference electrode. Figure 4a shows cyclic voltammograms of PEM (20/40/40 PEGDMA/SCN/LiTFSI) scanned at a rate of 1 mV/s between -0.5 and 6.0V vs. Li/Li⁺. Lithium plating and stripping are observed at a potential in the vicinity of -0.3V and 0.5V vs. Li/Li⁺ in the

cathodic and anodic scans, respectively. Two oxidation peaks appear at around 4.3V and 5.5V vs. Li/Li^+ in the anodic scans, followed by two reduction peaks at around 1.3V and 1.7V vs. Li/Li^+ in the subsequent cathodic scans. The reduction peaks become more pronounced with repeated cycles. This suggests that PEM (20/40/40 PEGDMA/SCN/LiTFSI) could hardly withstand the high voltage of 6.0V vs Li/Li^+ . In Figure 4b, PEM (20/40/40 PEGDMA/SCN/LiTFSI) shows better stability when being cycled between -0.5V and 4.5V vs. Li/Li^+ . According to He et al [48], PEM based on the PEGDA matrix exhibits greater stability up to 4.5V vs. Li/Li^+ . Hence, PEM (20/40/40 PEGDA/SCN/LiTFSI) was assembled into half-cells to further evaluate the battery performance. As depicted in Figures 5c, the specific capacity noticeably decays in the $\text{LiFePO}_4/\text{PEM}(20/40/40 \text{ PEGDA/SCN/LiTFSI})/\text{Li}$ half-cell, but it appears slightly more stable in the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PEM}(20/40/40 \text{ PEGDA/SCN/LiTFSI})/\text{Li}$ half-cell (Figure 5d), showing about 15~20% decay at 50th cycle tested. The Columbic efficiency remains stable for both half-cells and thus it met most requirements for cathode in low-to-moderate power lithium ion battery applications.

Future perspectives

The present solid state, superionic polymer electrolyte membranes are flame-retardant and compatible to LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes, and thus meet most criteria for the secondary lithium ion battery application in portable devices. However, for high energy and high power density application in EVs, it requires higher storage capacity via increasing the surface areas of cathode and anode materials using mesoporous electrodes. It can be anticipated that surface modifications of nanoscale carbonaceous electrode materials such as CNT, GO, silicon anodes as

well as sulfur or multicomponent metal oxides such as $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathodes, will play pivotal roles to further afford higher energy and power density.

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