

Fire retardant, superionic solid state polymer electrolyte membranes for lithium ion batteries

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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 $\text{Li}_4\text{Tl}_5\text{O}_{12}$ electrodes against lithium foil counter electrode and their future prospects are discussed.

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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^{*},8–10]. 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 [13,14,15,16]. 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 [28,29,30]. 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, that is, 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 [31,32,33] 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.

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