

Research on a gel polymer electrolyte for Li-ion batteries*

Guangchao Li, Zhaohui Li, Peng Zhang, Hanping Zhang,
and Yuping Wu[‡]

*Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis
and Innovative Materials, Fudan University, Shanghai 200433, China*

Abstract: The preparation, physical, and electrochemical properties of Li-ion conducting membranes, poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)]-based gel polymer electrolytes, are briefly reviewed in this paper. Phase separation or inversion method is mostly used to prepare microporous membranes because of the flexibility of its operation and controllable pore structure. The crystallinity of the polymer matrix and the pore structure of the membrane are the key issues to prepare P(VDF-HFP)-based gel polymer electrolytes with high Li⁺ conductivity and good mechanical strength. As to their further directions, they are also discussed.

Keywords: P(VDF-HFP); microporous membranes; structure control; polymer electrolytes; lithium-ion batteries.

INTRODUCTION

Owing to the promising and very wide range of applications for Li secondary batteries, which provide higher output voltage, higher specific capacity, longer cycle life, improved safety, and so on, polymer electrolytes have been increasingly studied in recent decades [1–3]. Polymers including poly(ethylene oxide) (PEO) [4], polyacrylonitrile (PAN) [5–7], poly(methyl methacrylate) (PMMA) [8], poly(vinylidene fluoride) (PVDF) [9,10], and their copolymers such as poly(acrylonitrile-methyl methacrylate) [P(AN-MMA)] [11–14], poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] [15–17] have been used as polymer matrixes. As early as the 1970s, solid-state polymer electrolytes based on the complex of PEO and alkali metals salts have received great attention [18–20]. However, their ionic conductivity at room temperature is very low and is still inadequate for practical use at higher current densities, despite much research devoted to increasing their ionic conductivity by several orders of magnitude. For this reason, much recent attention has turned to gel polymer electrolytes, which can be regarded as an intermediate state between typical liquid electrolytes and dry solid polymer electrolytes. Gel polymer electrolytes usually exhibit ionic conductivity ranging from 10⁻⁴ to 10⁻³ S·cm⁻¹ at room temperature, near to that of commercial liquid electrolytes. In gel polymer electrolytes, the liquid component is trapped in the polymer matrix, thereby preventing leakage of liquid electrolyte from the polymer matrix. Consequently, the safety of Li-ion batteries is greatly improved.

Among various polymers, P(VDF-HFP) has been extensively investigated because of its high mechanical strength and chemical stability with respect to nonaqueous electrolyte and electrode materials since the first report by Bellcore Corp. in 1994 [21–23]. Several reviews on separators [24,25] and poly-

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[‡]Corresponding author: E-mail: wuyup@fudan.edu.cn

mer electrolytes [26,27] of Li-ion batteries have been published in recent years, but none gives special attention to the tremendous progress made in the development of P(VDF-HFP)-based gel polymer electrolytes.

This paper aims to review the latest developments in P(VDF-HFP)-based gel polymer electrolytes, including their basic properties, preparation, and modification. An attempt is made to highlight those key issues in previous work that have stimulated further research toward practical application in Li-ion batteries.

GENERAL PROPERTIES

As a polymeric matrix of gel electrolytes, polymers are needed to meet several requirements [15]: (1) good electrochemical stability toward oxidation and reduction at Li electrodes, (2) good compatibility with the liquid electrolyte, (3) sufficient thermal stability, (4) easy production at low cost, and (5) good mechanical strength of the final product.

Among several polymers, the family of P(VDF-HFP) copolymers was found to meet all the above-mentioned requirements. P(VDF-HFP) cannot dissolve in the liquid electrolyte (usually carbonates) owing to its strongly electron-withdrawing functional group ($-C-F$), which also provides good electrochemical stability and noncombustibility. Furthermore, it has a high dielectric constant ($\epsilon = 8.4$) that assists in greater ionization of Li salts, and thus providing a high concentration of charge carriers. In the polymer, the HFP units reduce the crystallinity, rendering its solubility in acetone and lowering its melting temperature [25]. As a result, the content of HFP units in P(VDF-HFP) also increases the uptake amount of liquid electrolyte due to considerable swelling of the polymers. The amount of the electrolyte solvent absorbed by P(VDF-HFP) at room temperature presents the following trend: DMC > EC/DMC > DEC > EC/DEC [27]. By the way, in order to absorb the liquid electrolyte, a porous structure is necessary.

Nonetheless, the most critical issue of the P(VDF-HFP)-based polymer electrolyte is its interfacial stability toward Li metal. In fact, fluorinated polymers are not chemically stable toward Li owing to an interfacial reaction between Li and $C-F$, which results in the formation of LiF and renders PVDF-based polymer electrolytes unsuitable for batteries using Li metal as anode. This phenomenon was confirmed via Li plating/stripping experiments [28,29]. As a result, the P(VDF-HFP)-based polymer electrolyte is used for Li-ion batteries, which use graphitic carbons as anode.

PREPARATION METHODS

The structure of the porous membranes has a decisive effect on ionic conductivity and solution leakage of the porous gel polymer electrolytes. The ideal membranes for gel polymer electrolyte based on P(VDF-HFP) should have high porosity and small pore diameter with narrow pore size distribution. The experiments show that the porosity should be about 80 % and pore diameter should be $<1 \mu\text{m}$ [30]. Therefore, to obtain such a porous structure becomes essential for good performance of the gel polymer electrolytes. Porous membranes of P(VDF-HFP) are generally prepared by: (1) casting method, (2) phase separation or inversion method, and (3) electrospinning [31–33].

Casting method

At an early time, films of gel polymer electrolyte were usually prepared by casting a mixture of the liquid electrolyte solution and a matrix polymer in a low-boiling-point solvent. In this process, the polymer matrix was dissolved into the solvent [tetrahydrofuran (THF), acetonitrile, etc.] together with a nonaqueous Li salt electrolyte. The resulting viscous solution (consisting of polymer matrix, low boiling solvent, and liquid electrolyte) was cast. After the low boiling solvent was volatilized, gel electrolyte films were obtained. They are tacky and usually mechanically weak because of the presence of

the salt. Though many hybrid electrolytes exhibit high ionic conductivities, most of them present various demerits, which prevented their use in practical cells. For example, their mechanical properties are often very poor and the films have to be strengthened by either chemical or physical (high energy radiation) curing or cross-linking. Besides the need for cross-linking, the main shortcoming of the above process is that it has to be carried out in a completely moisture-free atmosphere because the moisture-sensitive Li salt is present at the initial stage. This critical atmosphere requirement has prevented its large-scale production.

To facilitate industrial production, a kind of extraction and activation method based on P(VDF-HFP) was successfully developed to produce porous polymer electrolyte for Li-ion batteries [21,22,34]. In this method, P(VDF-HFP) solvent such as acetone, and Li salt-free plasticizer such as dibutyl phthalate (DBP), are mixed and cast onto a carrier. Once the solvent is evaporated, plasticized films consisting of the polymer matrix and plasticizer can be obtained. Later, the DBP plasticizer is extracted with an appropriate solvent to prepare porous membranes, which provide much more mechanical integrity than direct casting the mixture containing Li salt. Then it is used as separator to assemble a battery, which is activated by adding liquid electrolyte in a dry room. The porous membrane is re-swelled and becomes gel polymer electrolyte. This process is quite similar to that of producing Li-ion batteries with the liquid electrolyte, which requires critical moisture control only during the last activation step. Thus, the application of polymer electrolyte becomes more feasible.

The most critical stages of this process are the plasticization of P(VDF-HFP) copolymers, subsequent removal of plasticizer, and the final re-swelling in an electrolyte solution. Solvents with low boiling points such as diethyl ether or methanol are successfully employed to remove DBP from the polymer matrix, leaving a pore structure in the polymer layers which is then refilled with the liquid electrolyte during the cell activation process. The ability of the previously extracted and dried P(VDF-HFP)/DBP laminates to re-swell after immersion in the organic electrolyte solutions is critical to their application in Li-ion batteries. The larger the amount of liquid electrolyte is trapped, the higher the ionic conductivity of the membrane has. The memory effect of pores during the removal of DBP is not 100 % effective. Accordingly, the liquid electrolyte uptake during the activation step is slightly lower than the initial volume occupied by DBP.

However, the DBP extraction step is inconvenient since it increases the cost of the process and presents safety concerns related to handling of a large volume of volatile solvents. Consequently, it is not well used after the finding of the following phase inversion method.

Phase inversion method

Phase separation/inversion is one of the most important methods to prepare microporous polymer membranes. It can be roughly classified into four forms: (1) precipitation in a nonsolvent—nonsolvent-induced (NIPS); (2) solvent evaporation—evaporation-induced (EIPS); (3) precipitation by absorption of nonsolvent from the vapor phase—vapor-induced (VIPS); (4) precipitation by cooling—thermally induced (TIPS). All the above processes are applicable to prepare P(VDF-HFP) membranes, but certain methods may be preferred for a specific case and only the most widely adopted two processes (NIPS and EIPS) are introduced here. Based on the ternary phase diagram of P(VDF-HFP)-solvent-nonsolvent system (Fig. 1), the composition of the polymer solution and nonsolvent significantly affects the structure of the membranes and size of the pores, thus resulting in varied thermal, mechanical, swelling, and electrochemical properties of the prepared polymer electrolytes.

In NIPS process, the polymer solution is coated on glass slide and immersed in nonsolvent. The polymer precipitates from the solution while the solvent is replaced by nonsolvent, and thin porous polymer films are produced. Applying oligomeric poly(ethylene glycol) PEG as additive, dimethylacetamide (DMAC) as solvent and water as nonsolvent, partially extracting of the PEG molecules during the phase inversion process can result in different porosities and following different ion conductivities [35].

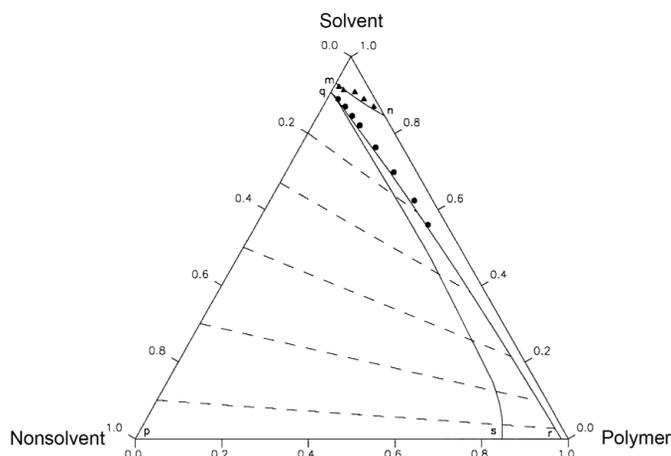


Fig. 1 Sketch of ternary-phase diagram for polymer–solvent–nonsolvent system. Line “mn”: crystallization line; line “pqr”: the binodal; line “pqs”: the spinodal [23].

The EIPS process to prepare microporous separators and laminated plastic Li-ion batteries which avoids the use of a plasticizer extraction process is as follows [15]. The copolymer is at first dissolved in a mixture of volatile acetone as solvent and ethanol as nonsolvent. The polymer solution is then cast onto a sheet to form a film. After drying in air, films with pores are obtained. When pentane is used as a nonsolvent, the polymer membrane exhibits smaller pore sizes (12 nm) and a higher BET surface area ($120 \text{ m}^2 \text{ g}^{-1}$) than those prepared using 1-butanol, whose pore diameter is 40 nm and BET surface area is $48 \text{ m}^2 \text{ g}^{-1}$ [36,37]. Using PEG as an additive (P(VDF-HFP):PEG = 1:1, w/w), the polymer membrane prepared with dimethylformamide (DMF) as solvent delivers higher discharge capacity than the membranes prepared with acetone as solvent [38].

The membrane structure also influences the performance of the gel polymer electrolytes. With phase inversion method, the structure of the membranes can be easily controlled by the composition of solution and processing conditions, two structures can be prepared: honeycomb- and network-like ones [30]. The latter structure with small pores and narrow pore distribution can prevent the leakage of liquid, and its high porosity is good to achieve high ionic conductivity, which is $>10^{-3} \text{ S cm}^{-1}$ when immersed in 1 mol l^{-1} LiClO_4 solution of EC/PC(1:1, v/v) to form gel polymer electrolytes. This kind of process has advantages of low cost and little pollution. The resulting gel polymer electrolytes have good electrochemical stability and are suitable for the application of Li-ion batteries.

EIPS and NIPS can be combined for the preparation of P(VDF-HFP)-based microporous membranes [17]. P(VDF-HFP) and polyvinyl alcohol (PVA) was dissolved in DMF. The resultant viscous solutions were spread as a thin film on a glass substrate. The film was dried at $80 \text{ }^\circ\text{C}$ in vacuum for 5 h to facilitate DMF evaporation. Then, the film was immersed in deionized water at $60 \text{ }^\circ\text{C}$ to remove PVA from P(VDF-HFP) matrix to form microporous structure. P(VDF-HFP)-based membrane prepared by this way can get high porosity and electrolyte uptake of 85.9 and 89.6 %, respectively, and the ionic conductivity can be up to $7.94 \times 10^{-3} \text{ S cm}^{-1}$.

Electrospinning

The electrospun membrane appears to be particularly suitable for use as a host matrix in microporous polymer electrolytes because the fully interconnected pores with large surface area can function as efficient channels for ion conduction [39–42]. The first report of such an application of the electrospun PVDF membrane for Li-ion battery was disclosed in 2003 (Fig. 2) [43]. Subsequent studies in this area

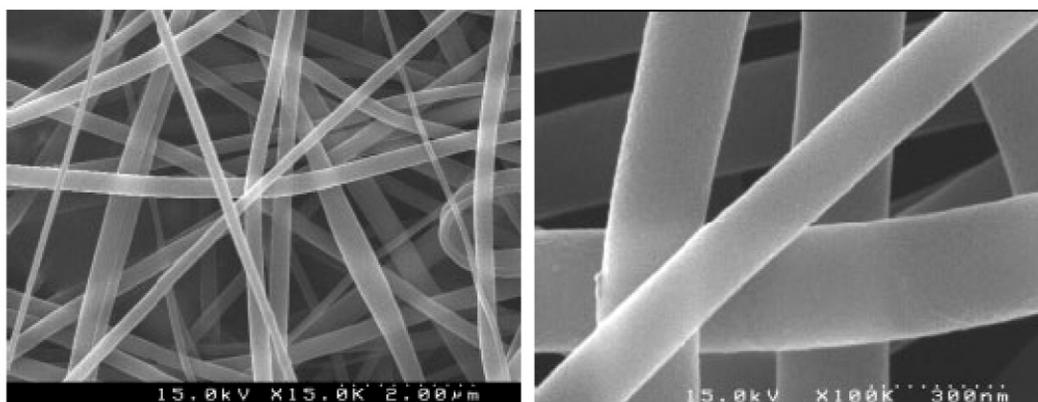


Fig. 2 SEM micrographs of PVDF nanofibrous membrane obtained by electrospinning [43].

were focused on the suitability of electrospun membranes of PVDF, P(VDF-HFP), and PAN for Li-ion battery applications [44–46].

P(VDF-HFP) fibrous membranes can be prepared by electrospinning of the polymer solution in a mixed solvent of acetone and DMAc [33]. The fibrous membrane prepared under the optimized conditions of 16 wt % solution in acetone: DMAc (7:3, w/w) at 18 kV presents uniform morphology and an average fiber diameter of 1 μm and the ionic conductivity is above $10^{-3} \text{ S cm}^{-1}$.

MODIFICATION

There are at least three phases in the microporous P(VDF-HFP)-based gel polymer electrolyte: (1) a semi-crystalline polymer with a relatively low degree of crystallinity which is not swollen and hardly conducts ions, (2) an amorphous part which is plasticized by electrolyte solution, and (3) micropores filled with liquid electrolyte. When the bulk of the membrane is composed of connected micropores, the ion conductivity of the gel polymer electrolyte mainly depends on the property of the liquid electrolyte. Otherwise, if the prepared membrane does not have many connected pores, the transfer of Li^+ mainly happens in the plasticized swelled P(VDF-HFP). Therefore, modifying the pore structure of the membrane and changing the crystallinity of the polymer matrix have been developed as the most important strategies to prepare P(VDF-HFP)-based gel polymer electrolyte with both high Li^+ conductivity and good mechanical strength. The former is mainly achieved by optimizing the preparation conditions and the latter by modifications of polymer matrix, such as blending, copolymer and cross-linking, compounding, and adding nanofillers.

Blending

Amorphous polymer electrolytes conduct ions via segmental movement of the polymer chains at temperatures above their glass transition temperature (T_g). Consequently, promoting the segmental mobility of the polymer chains by decreasing the T_g is an effective method to increase the ionic conductivity. The concept of blending a soft conductive polymer component with a mechanically stable polymer [PVDF/P(VDF-HFP)] to gain high ion conductivity is an attractive approach to polymeric electrolytes where high conductivity is combined with mechanical stability. For this purpose, PAN, PEO, PMMA, and their copolymers such as poly(ethylene carbonate-co-ethylene oxide) [P(EC-EO)], poly(methyl methacrylate-co-acrylonitrile-co-lithium methacrylate) (PMAML), and polyethylene oxide-co-polypropylene oxide-co-polyethylene oxide (P123) are preferred polymers to blend with P(VDF-HFP).

Blends of P(VDF-HFP) and PMMA grafted with P(EC-EO) forms homogeneous membranes, which are doped with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) salt, exhibit T_g values between -46 and -28 °C, which increases with the LiTFSI salt concentrations [47]. These membranes reached ionic conductivities of $6.3 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 20 °C. The addition of 20 wt % P(VDF-HFP) in the mixture leads to an increase of T_g by about 5 °C in comparison to the corresponding homogeneous membranes, irrespective of the salt concentration. It was found that an increase in the salt concentration of the blend membranes does not change the compatibility of the two blend components, but decreases the crystallinity of P(VDF-HFP).

The weight ratio of P(VDF-HFP) to PAN was optimized at 80:20, and the resulting gel polymer electrolytes have an electrolyte solution uptake of about 80 % by weight and exhibit high ionic conductivity $>10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. The decomposition voltage of these gel polymer electrolytes is about 4.6 V vs. Li^+/Li [48]. However, the cells assembled employing these gel polymer electrolytes showed poor cycling life and high-rate performance. The main reason is primarily due to the reaction of Li with $-\text{CN}$ groups in PAN, which leads to gradual increases of the internal resistance of the cell.

Polymer electrolytes based on the blend of PMAML and P(VDF-HFP) exhibit an ionic conductivity up to $2.6 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature [49]. Though the interfacial resistance between the polymer electrolyte and Li electrode increases with the storage time, it decreases after the surface of Li is refreshed by means of cyclic voltammetry or galvanostatic charge.

When P123 was blended with P(VDF-HFP), mesopores with well-defined sizes were formed [50]. The ionic conductivity at room temperature of the polymer electrolytes comprising P(VDF-HFP)/(P123) blend, EC/PC, and LiClO_4 increases with the content of P123 and is up to $4 \times 10^{-3} \text{ S cm}^{-1}$ when the weight ratio of P123 to P(VDF-HFP) is 70 %, at which big channels were formed in the hybrid polymer membrane. These polymer electrolytes are electrochemically stable up to 4.5 V (vs. Li^+/Li).

Copolymerizing and cross-linking

When the porosity of the membrane is large, a lot of liquid electrolyte is absorbed to achieve high ionic conductivity, and the mechanical properties of the prepared gel polymer electrolytes will be sacrificed [37,51]. As a result, the mechanical strength of the gel polymer electrolyte should be increased. Fortunately, microphase-separated polymer electrolyte comprising two polymers, one with very good affinity for polar solvent to facilitate electrolyte swelling and the other with poor affinity so that structural integrity and mechanical strength can be maintained [52], is promising in solving this problem.

Porous polymer membranes made of P(VDF-HFP)-chlorotrifluoroethylene (CTFE) terpolymers have been fabricated from a range of solvents/nonsolvent systems [53]. Though it shows little difference with P(VDF-HFP) at room temperature, significant uptake of 112 wt % EC/PC (2:1, wt/wt) solvent, good ionic conductivity and good structural integrity at 60 °C have been observed.

When a kind of co-continuous polymer blend electrolytes using PEG, methacrylate macromonomers, and P(VDF-HFP) was prepared, the components were found to take place a phase separation during the casting process [47]. After the macromonomer was subsequently polymerized by UV-irradiation, the resulting morphology was a three-dimensional matrix of P(VDF-HFP) with continuous phase of ionically conductive PEG-grafted polymethacrylate networks. The ionic conductivities of the P(VDF-HFP)-PEG membranes are in the order of 10^{-4} , 10^{-3} , and $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at temperatures of -30 , 25, and 50 °C, respectively [38].

The tensile modulus and flexibility of the membrane can be improved by combination of PEG dimethacrylate (PEGDMA) network and P(VDF-HFP) copolymer chain, which is plasticized by PEG. The cross-linked polymer membrane with composition of P(VDF-HFP)/PEG/PEGDMA= (5/3/2) shows electrolyte uptake of 98.2 % and ionic conductivity $> 1.0 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature in the presence of 1 M $\text{LiPF}_6/\text{EC-DEC}$ [54]. This gel electrolyte can form a stable passivation layer on the

Li metal surface, and the cross-linked gel electrolyte assures electrochemical stability up to 5.0 V vs. Li/Li⁺.

Compounding

Another approach to get a balance between good affinity and mechanical strength is by applying micro-porous polyolefin such as polyethylene (PE) and polypropylene (PP) membrane to reinforce P(VDF-HFP) [55–57] since it is well known that gelled P(VDF-HFP) polymer matrix exhibits good affinity with electrolyte and polyolefin membrane has excellent mechanical strength. Polymer gel electrolytes based on P(VDF-HFP), Li salt, and carbonate solvents supported with a microporous polyolefin membrane for Li-ion polymer batteries show excellent mechanical properties and good adhesion toward electrodes and exhibit high ionic conductivity in the order of 10^{-3} S cm⁻¹ at room temperature. The membrane-supported gel polymer electrolytes were electrochemically stable up to 5.0 V vs. Li⁺/Li.

Adding nanofillers

It has been known that the addition of nano inorganic fillers such as magnesium oxide (MgO), titania (TiO₂, rutile or anatase), alumina (Al₂O₃), silica (SiO₂), LiAlO₂, zirconium dioxide (ZrO₂), carbon nanotubes (CNTs), and other fine particles like clay and kaolin to the polymer electrolyte results in the improvements of ionic conductivity as well as mechanical and electrochemical properties [58]. The system can be described as a heterogeneous, phase-separated, plasticized polymer electrolyte.

MgO-based gel polymer electrolytes work well with both positive and negative electrodes [59]. An ionic conductivity of about 0.4×10^{-3} S cm⁻¹ was calculated for the MgO-based gel polymer electrolyte containing 40 % 1 M solution of LiPF₆ in EC/DMC (1:1, v/v). Self-standing Li-ion cells were constructed using the MgO-based gel polymer electrolyte, and the resulting Li-ion battery showed good cycling behavior.

The TiO₂ nanoparticles in the gel polymer electrolyte play useful roles in increasing the ionic conductivity and the cation transference number. The addition of TiO₂ nanoparticles to the P(VDF-HFP) polymer matrix leads eventually to the improvement of the mechanical strength and the keeping of the polymeric feature even for high filler content. Also, it may provide low liquid uptake but adequate ionic conductivity by some dipole interaction of rutile TiO₂ with the polymer matrix [60]. Excellent electrochemical stability of the polymer electrolyte is attained for the electrolyte with 10–60 wt % TiO₂ (Fig. 3). The ion migration within nanopores may be promoted by TiO₂ with higher dielectric constant, which is originated by its inherent dipole property. Relating to this role of TiO₂, it is well agreed that the nanoparticles can diminish the ion-aggregation in the electrolyte medium, which can be originated from their dielectric nature and/or the chemical interaction between TiO₂ and P(VDF-HFP).

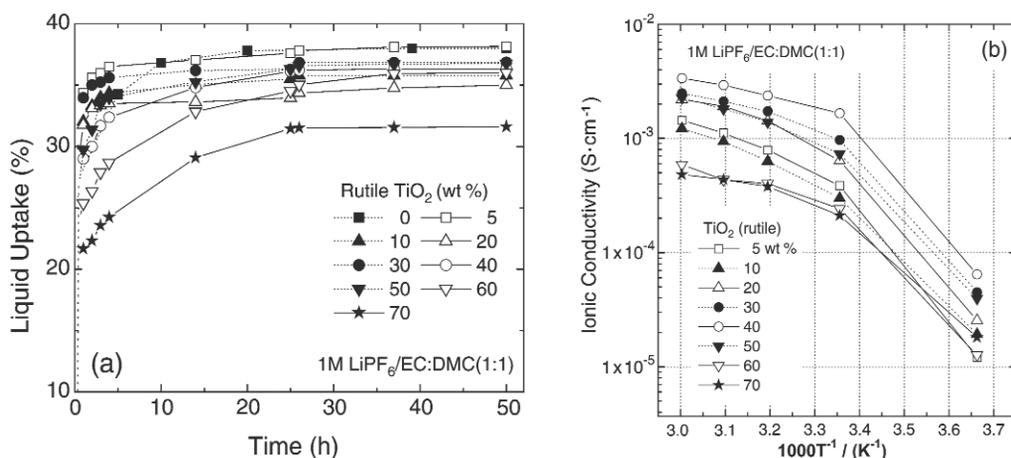


Fig. 3 (a) Liquid uptakes of the P(VDF-HFP)/TiO₂ (rutile) films, determined by the difference in weights before and after absorbing the electrolyte solution of 1 M LiPF₆/EC/DMC (1:1) and (b) temperature dependence of ionic conductivity for the polymer electrolytes as functions of TiO₂ content [60].

Various amounts of alumina (Al₂O₃) nanoparticles were used as fillers in the preparation of porous polymer membrane based on P(VDF-HFP) [62]. The crystallinity of polymer matrix decreases with the addition of Al₂O₃ nanoparticles, and the amorphous phase expands accordingly. The resulting polymer electrolyte has an ionic conductivity of $2.11 \times 10^{-3} \text{ S cm}^{-1}$, the Li-ion transference number of 0.66 and the activation energy for ions transport of $4.816 \text{ kJ}\cdot\text{mol}^{-1}$ when the gel polymer matrix contains 10 wt % Al₂O₃ nanoparticles (Fig. 4).

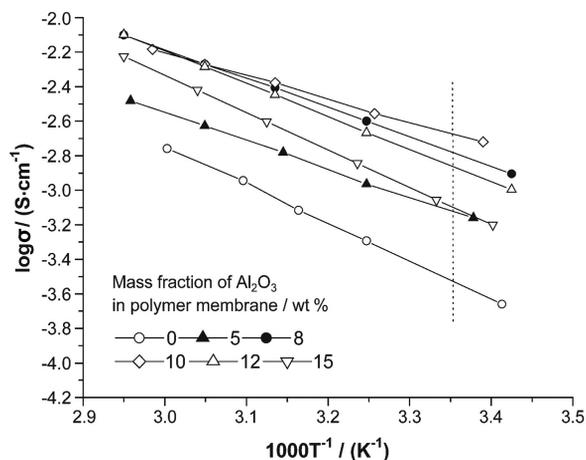


Fig. 4 Log $\sigma - 1/T$ curves of P(VDF-HFP) polymer electrolyte filled with various amounts of Al₂O₃ nanoparticles [62].

In microporous polymer electrolyte, the Li ions migrate not only in gel electrolyte but also in liquid electrolyte. The former is slow while the latter is fast. Nanopores by the interaction of nanoparticle or its surface groups with shrinking polymer matrix may be formed during the preparation of highly filled polymer membrane. The increase of the porosity of polymer film improves the absorption ability of nonaqueous electrolyte, thus facilitating the migration of Li ions. At the same time, the competition

(i.e., Lewis acid–base effect) between O atoms of Al_2O_3 and F atoms of polymer chain with respect to Li ions in the region of the gel electrolyte weakens the complexation of F atoms with Li ions [61]. Both effects lead to the higher Li-ion conductivity and lower activation energy for Li-ion transport.

Application of fumed silica as inorganic filler to the copolymer membranes allows for a very pronounced increase in ionic conductivity of the resulting gel polymer electrolytes [34]. This phenomenon can, to a large extent, be attributed to enhanced electrolyte uptake ability of the microporous membrane caused by the existence of highly dispersed ceramic phase, which allows absorption of more liquid electrolyte.

To increase the ionic conductivity of gel polymer electrolytes based on P(VDF-HFP), surface modification of silica by various silane agents has been tried [63,64]. The stability characteristics for the gel polymer electrolytes containing two kinds of modified silicas (with methacryloxy and vinyl functionalities), as well as for those without any silica filler is compared. The surface modification can increase not only ionic conductivity but also interfacial stability.

P(VDF-HFP)- ZrO_2 based composite membrane soaked in 1 M LiClO_4 electrolyte solution containing 1:1 (v/v) ratio of EC and DEC exhibits maximum ionic conductivity as high as $11.04 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature [17,65], which is close to the liquid electrolyte itself.

CNTs represent an important group of nanomaterials with attractive electronic, chemical, and mechanical properties. When 2 wt % multiwall carbon nanotubes (MWCNTs) were used as filler in electrospun P(VDF-HFP) membranes to form a gel electrolyte [66], the gel polymer electrolyte shows an ionic conductivity of about $5.85 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and an improved interfacial stability.

Though the optimal filler content varies in a large range from 2 to 40 wt % when the composite gel electrolytes exhibit best performance according to different filler types, it seems that it is not the filler type but the size distribution or surface area of the filler and its affinity with P(VDF-HFP) polymer matrix that play the key role in defining the performance of the gel polymer electrolytes.

SUMMARY

Due to its inherent excellent properties and easy access, P(VDF-HFP)-based polymer electrolyte has attracted great interest from researchers and engineers since its introduction in 1994, and is becoming a promising industry. Several methods such as adding nanofillers have been applied to prepare a porous membrane based on P(VDF-HFP) copolymer with well-ordered structure and high ion conductivity, which is critical for application in Li-ion batteries [67,68]. However, the cost and qualification yield of the processes are also crucial for practical application, which needs further exploring so that the ratio of performance/cost of the gelled polymer electrolytes can compete with that of the traditional microporous PP or PE separators. Of course, the research and development on P(VDF-HFP)-based gelled polymer electrolytes will continue, and the control of porosity and stacking structures will be another focus [8,69]. After finding low-cost and reliable processes, their large-scale application will be realized soon [70].

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