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REVIEW

Polymer Electrolytes Integrated with Ionic Liquids for Future Electrochemical Devices

Moon Jeong Park,[1,2] Ilyoung Choi,[2] Jaewan Hong,[2] Onnuri Kim[2]

[1]Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

[2]Division of Advanced Materials Science (WCU), Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

Correspondence to: M. J. Park (E-mail: moonpark@postech.edu)

ABSTRACT: The global energy crisis and an increase in environmental pollution in the recent years have drawn the attention of the scientific community towards the development of efficient electrochemical devices. Polymers containing charged species have the potential to serve as electrolytes in next-generation devices and achieving high ion transport properties in these electrolytes is the key to improving their efficiency. In this article, we explore ways to improve the ion transport properties of solid polymer electrolytes by focusing on the use of ionic liquids (ILs). The application of IL-incorporated polymer electrolytes in lithium batteries, high temperature fuel cells, and electro-active actuators is summarized. For each system, the current level of understanding of the diverse factors affecting the transport properties of polymer electrolytes integrated with ILs is presented, in addition to the challenges encountered and strategies toward obtaining significantly improved device performances. The creation of self-assembled morphologies in IL-containing polymer electrolytes by the use of block copolymers is particularly highlighted as a novel prospective technique geared towards obtaining next-generation electrochemical devices with enhanced performances. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2363–2376, 2013

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INTRODUCTION

Recently, ionic liquids (ILs) composing organic cations and counterions have received enormous interest in various research areas, including catalysis,[1] inorganic particle synthesis,[2] and vacuum technologies.[3] This is attributed to the fascinating physiochemical properties of ILs, such as negligible vapor pressure and large thermal and electrochemical stability window.[4] ILs have particularly emerged as important materials in the era of electrochemistry owing to the prospects of offering efficient ion conduction and can be used as powerful electrolytes in diverse electrochemical devices.[5,6]

Many electrochemical devices now require solid-state ionic conductors. Nevertheless, practical applications have been limited to the use of liquid-state electrolytes to ensure efficient ion transport.[7] One way of developing solid-state electrolytes using ILs is by employing mechanically supportive matrix materials that incorporate ILs. Among various candidate materials, polymers show promise to be used in electrolytes owing to their flexibility and ease of fabrication at low costs. Depending on the types of applications, polymers can be designed to conduct specific ions: examples of such polymers include poly(ethylene oxide) (PEO), which exhibits the ability to transport lithium ions;[8–10] acid-tethered polymers, which offer the prospect of conducting protons.[11,12] Consequently, the ion transport properties of polymers containing ILs have been subjected to extensive studies lately, indicating that the synergetic actions between the ILs and the polymer matrices are crucial for achieving improved transport properties.[13–15]

Among the various electrochemical devices, ILs-integrated polymer electrolytes can be successfully applied to lithium batteries, high temperature proton exchange fuel cells (PEMFCs), and electro-active actuators. These days, the development of solid electrolytes that can replace liquid electrolytes in lithium batteries has become an urgent requirement. The requirement is driven by the need to improve the safety, simplify the manufacturing process with flexible design, and to achieve electrochemical stability at high cell potential.[15–17] It also offers exciting possibilities for the development of future high-energy lithium batteries by enabling the direct use of lithium metal at the anode.[18,19] Although solid-state electrolytes provide many future prospects, the major limitation in utilizing them in lithium batteries is their relatively low conductivity when compared to liquid electrolytes.[20,21] Thus, research is now focused on obtaining IL-impregnated polymer electrolytes with improved ionic conductivity and optimized mechanical stability.[22–24]

Among various strategies to develop novel solid ionic conductors for lithium batteries, obtaining polymer electrolytes with phase-separated morphologies at nanometer scales have received special attention. This is because non-conducting phases can provide effective mechanical support, while the ion transport can take place along the well-arranged conduction domains.[23,24] Particularly, the selective incorporation of ILs into the conducting phases is considered effective in enhancing the conductivity without impeding the mechanical stability offered by the non-conducting domains.[24,25]

Over the past few decades, PEMFCs are being developed for portable electronic devices and vehicles for operation under conditions of low temperatures (<80°C) and high humidity.[12,24,26] Sulfonated polymers such as Nafion™ [12,27] and sulfonated polyaromatic engineering plastics[28,29] have been served as polymer electrolytes in PEMFCs owing to their high proton conductivity under the above-mentioned conditions. Despite extensive research efforts, the commercialization of PEMFCs appears distant, which has stimulated a demand for operation at temperatures above 120°C in recent years.[29,30] The major benefits of high operation temperature are the improved long-term stability of platinum catalyst and enhanced reaction kinetics at the electrodes. Unfortunately, the operation at temperatures above the boiling point of water results in the excessive drying of most sulfonated polymers, which causes a large reduction in the proton conductivity of the membranes.[31,32] Polymer electrolytes containing protic solvents have been conventionally used to obtain efficient proton conduction under dry conditions.[33,34] However, the lifetime of the devices employing these electrolytes is limited owing to the disruptive characteristics.

These issues may be solved by the use of ILs that are nonvolatile and have nondisruptive characteristics as the transport properties of IL-incorporated polymers are extensively examined in recent years by employing a variety of combination polymers and ILs.[14,35–37] In the case of ILs, the choice of cations and anions plays an important role in determining the conductivity of IL-integrated polymers, which is attributed to the dissimilar polarities and diffusion coefficients of the ions.[35,37,38] For polymers, the structure-property relationship has attracted most attention and the various observations related to the dependence of the conductivity on the polymer chain architecture and morphology have motivated the controlled synthesis of polymers with random,[39,40] block,[14,35–38] or graft configurations.[41]

As the last category, electro-active actuators made of ionic polymers that show reversible deformation under an applied voltage have been extensively studied till date for application in robotics[42] and as artificial muscles.[43] Such actuators can be classified into bucky-gel actuators,[44] actuators based on interpenetrating polymer network,[45] and actuators composed of ionic polymer-metal composites.[46] Among them, bucky-gel actuators, which possess a layer of polymer electrolyte sandwiched between two electrodes composed of single-wall carbon nanotubes (SWNTs) containing ILs, have particularly attracted immense interest.[44,47–53] Early studies on polymer electrolyte layers of the bucky-gel actuators had focused on dry ionomers, which typically require activation fields in range 2–5 V.[42] It has been found that there is considerably more scope for producing higher levels of strain; for example, incorporating ILs into the dry polymers provided a huge increase in the performance of these devices.[47,48]

The bending mechanism in electro-active actuators comprising IL-integrated polymer electrolytes involves the migration of cations and anions toward the opposite electrodes in the presence of activation fields.[48,49] The relative sizes of the cations and anions in the ILs play an important role in determining the volume changes of each electrode, which in turn determine the level of strain (i.e., displacement) under a given applied voltage.[50,51] There are several other factors including the polarity and mobility of ILs within the polymer matrix that affect the actuation performance.[52,53] The limitations of conventional actuators can be placed on the slow switching times and the requirement of high driving voltages, which are critical drawbacks for biomimetic applications. However, no systematic work has been carried out yet to advance the technology toward obtaining rapidly responding and low-voltage driven electro-active actuators.

In this article, we describe the application of IL-incorporated polymers in lithium batteries, high temperature fuel cells, and electro-active actuators. Recent progress in advancing device performance by using various ILs and polymers will be summarized. In first section, we describe recent research efforts that have been taken to develop efficient all-solid-state lithium batteries by employing IL-integrated polymer electrolytes. Then, the challenges encountered in the practical application of polymer electrolytes containing ILs in next-generation lithium batteries will be addressed. In the subsequent section, we will review the new approaches to apply IL-incorporated polymers in PEMFCs operating at high temperature. Strategies to improve both mechanical properties and anhydrous conductivities will be described. In the final section, the recent advances in the fabrication and application of ionic polymer actuators comprising IL-embedded polymer electrolytes will be detailed. We have attempted to understand the importance of making an appropriate choice of ILs and polymers with suitable molecular designs in enhancing the actuation performance, on the basis of which we will make suggestions for approaches towards developing efficient electro-active actuators.

LITHIUM BATTERIES

The essential requisite of IL-incorporated polymer electrolytes for their use in lithium batteries is to achieve high Li^+ conductivity, which is intimately related to the lithium storage capacity and specific energy of the batteries. Hence, the extensive studies on IL-integrated polymer electrolytes have focused on the achievement of high Li^+ conductivity by combining various types of polymers and different ILs.[54,55]

As observed by many research groups, the addition of ILs into polymer electrolytes results in increased Li^+ conductivity because ILs can act as a plasticizer to help the fast relaxation of polymer chains, i.e., the lowering of the glass transition temperature (T_g) of the polymers.[24,56] The ILs uniquely differ from conventional nonionic plasticizers in their ability to manipulate ion transport mechanisms by altering the degree of Li^+ transference number in systems,[57,58] which leads to the substantial augmentation of the conductivity of the polymer electrolytes. In addition, the use of ILs allows accessing a wide electrochemical stability window and excellent thermal stability,[55] which are crucial for application in batteries.

Role of the Type of IL in Enhancing the Conductivity of IL-Incorporated Polymer Electrolytes

PEO-based polymers[8–10,15] and poly(vinylidene fluoride-*co*-hexafluoropropene) (PVdF-HFP)[60,61] are the most widely employed polymers in lithium batteries. The common cations in ILs fall into one of following three categories: alkyl pyrrolidiniums,[15,18] alkyl imidazoliums,[62–64] and alkyl sulfoniums.[65,67] The types of anions vary. When the aforementioned ILs were incorporated into Li salt-doped PEO and/or PVdF-HFP, the improved conductivity in the range 10^{-4}–10^{-3} S/cm was achieved,[15,18,62,63,65] which exceeds the well-known conductivity limits of dry polymer electrolytes[67] but are yet lower than that of conventional liquid electrolytes.[20,21]

As key parameters to improve the Li^+ conductivity of IL-integrated polymer electrolytes, the increase in the effective number of lithium ions and high Li^+ transference number are required by increasing the dissociation level of lithium salts in the IL-containing polymers.[68] This is closely related to the free energy of the polymer electrolytes containing ILs and is significantly affected by the types of cations and anions in the ILs. This idea prompted extensive research efforts to understand the effects of the types of ILs on the electrochemical properties of IL-impregnated polymer electrolytes typically by employing a wide range of anions in the ILs, while maintaining a single type of cations in the ILs.[64,66]

Fisher et al. investigated the transport properties of PEOs upon incorporating various ILs comprising five different anions while the alkyl sulfonium was fixed as the cation.[66] The studies revealed that the differences in the type of anion resulted in varying conductivities that differed by a few orders of magnitude, which has been attributed to the significant changes in solvation dynamics,[69] strength of ionic interaction,[70] and polymer relaxation motions.[71] This implies that the Li^+ transport mechanism in IL-containing polymers can be largely manipulated by the choice of the ILs.

Analogous results were obtained in the case of PVdF-HFP copolymers containing alkyl imidazolium-based ILs, in which the conductivity with the use of hexafluorophosphate, $[PF_6^-]$, was an order of magnitude higher than that obtained with tetrafluoroborate, $[BF_4^-]$.[64] This is particularly intriguing, since the ionic conductivity of the neat IL comprising $[PF_6^-]$ was lower than that of the IL containing $[BF_4^-]$. Therefore, we can conclude that the conductivity of polymer electrolytes incorporating ILs is not necessarily associated with the intrinsic properties of the ILs.

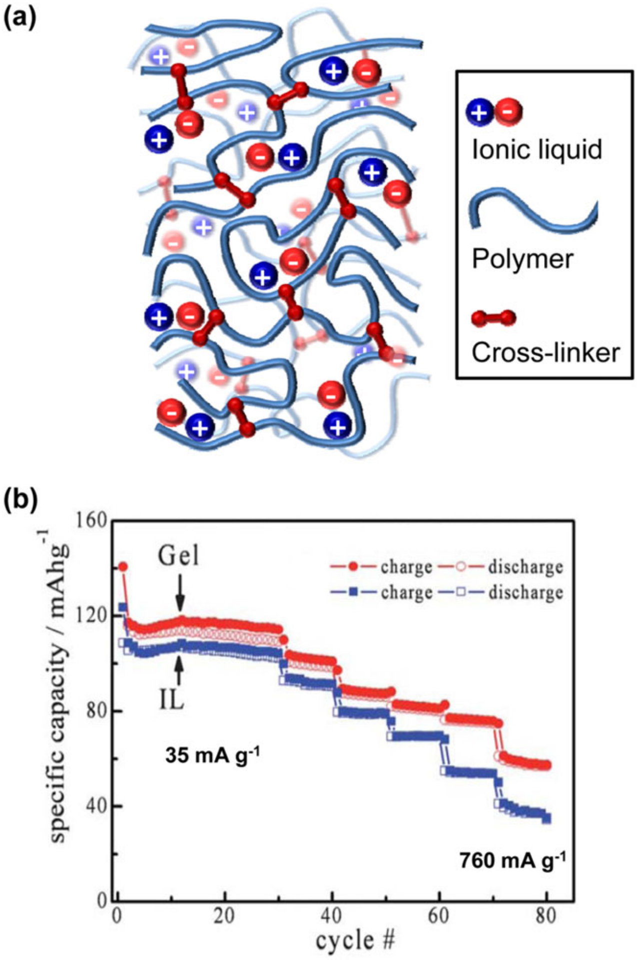


Figure 1. (a) Schematic illustration of cross-linked IL-incorporated polymer electrolytes and (b) the cycling performance of a battery comprising Li metal/the cross-linked IL-embedded polymer electrolytes/MWCNT-coated $LiFePO_4$. For comparison the cycling performance of a battery containing neat IL is also shown in (b). Figure 1(b) is adapted from Ref. [75] with the permission of Royal Society of Chemistry. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effects of Polymer Structures on the Electrochemical Properties of IL-Incorporated Polymers

Although PEO and PVdF-HFP are conventionally used in lithium batteries,[8,10,60] there is a rising demand for new types of polymers in order to establish a synergetic means of improving the electrochemical properties of IL-incorporated polymer electrolytes. Particularly, the commercially employed low-molecular-weight PEOs intrinsically exhibit poor mechanical properties, which potentially lead to fatal flaws in dendritic shorts.[72,73]

In this aspect, cross-linking of IL-incorporated polymer electrolytes has been commonly implemented,[22,74–76] as illustrated in Figure 1(a), as a straightforward process to increase the IL content to increase the ionic conductivity without losing the mechanical stability. The cross-linking reaction can be carried out in many ways. For example, the PEO chains can be readily cross-linked in the presence of photo-initiators after incorporating desired amounts of ILs.[76] Alternatively, hyper-branched PEOs can be used with the aid of cross-linkable moieties to produce a highly conducting IL-integrated polymer framework whilst preserving the mechanical strength.[22,74] The diverse cross-linking approaches have demonstrated high capacity, improved cyclability, and rate capability in batteries, which surpass the results obtained with neat ILs.[75] In Figure 1(b), the cycling performance of a battery containing cross-linked IL-incorporated polymer electrolytes is shown, compared to that of neat IL.

To optimize the conductivity and mechanical properties of the IL-incorporated polymer electrolytes, significant efforts have recently been devoted to the synthesis and characterization of PEO-based block or graft copolymers comprising mechanically robust polymer chains, i.e., poly(styrene-b-ethylene oxide) (PS-PEO).[23,24,77] This is due to the fact that Li^+ conducting pathways can be provided by the PEO chains with the PS chains imparting the mechanical stability up to 100°C. Particularly, observations on the effects of nanoscale morphologies of polymer electrolytes on Li^+ conductivity have motivated the research on nanostructured polymer electrolytes.[9,23,78] For example, the use of nanostructured poly(ethylene oxide-b-methyl methacrylate) (PEO-PMMA) block copolymer, can increase the Li^+ transference number to values up to 0.9 at room temperature, which is in sharp contrast to the low values exhibited by PEO-based polymers in the range 0.2−0.5.[78]

In order to optimize the mechanical stability and ionic conductivity of nanostructured polymer electrolytes, Park et al. recently investigated the morphologies and electrochemical properties of IL-incorporated PS-PEO electrolytes.[24] The dry PS-PEO exhibited microphase separated lamellar morphology with a periodicity of ca. 50 nm. Interestingly, the incorporation of small amounts of ILs (10 wt %) resulted in significant increment (3–5 times) in the ionic conductivity, as shown in Figure 2(a). This was accompanied by the enhanced segregation strength between the ion-containing PEO domains and the nonconducting PS domains, as observed by sharp interface between the two. This observation has been attributed to that the exclusion of the ILs by the nonconductive PS microdomains, which resulted in the production of a higher local IL concentration in the conductive PEO phases, which eventually facilitated fast ion transport by confinement effects. A schematic illustration of Li^+ transport along the IL-incorporated PEO domains of nanostructured PS-PEO block copolymer electrolytes is shown in Figure 2(b).

Note in passing that the use of triblock copolymer architectures rather than diblock copolymers may be beneficial in achieving better mechanical stability by creating the physical cross-links, as investigated by Lodge et al.[13,25] In addition, rather than a lamellar morphology, achieving an ideal morphology having cocontinuous ionic domains is perhaps worthwhile to pursue for the access of improved conductivity.[9] Recently, an approach to design IL-containing polymer electrolytes possessing cocontinuous ionic domains has been demonstrated by employing surface functionalized inorganic nanoparticles along with IL polymer brush.[79] A face-centered cubic morphology was derived, which showed considerably high ionic conductivity values in the range of 10^{-3}–10^{-2} S/cm at 5–85°C, which was attributed to the formation of continuous conducting channels on the nanometer scale. It is thus clear that the optimization of conductivity and mechanical properties of IL-containing polymer electrolytes using self-assembly could offer exciting possibilities for their use in future lithium batteries.

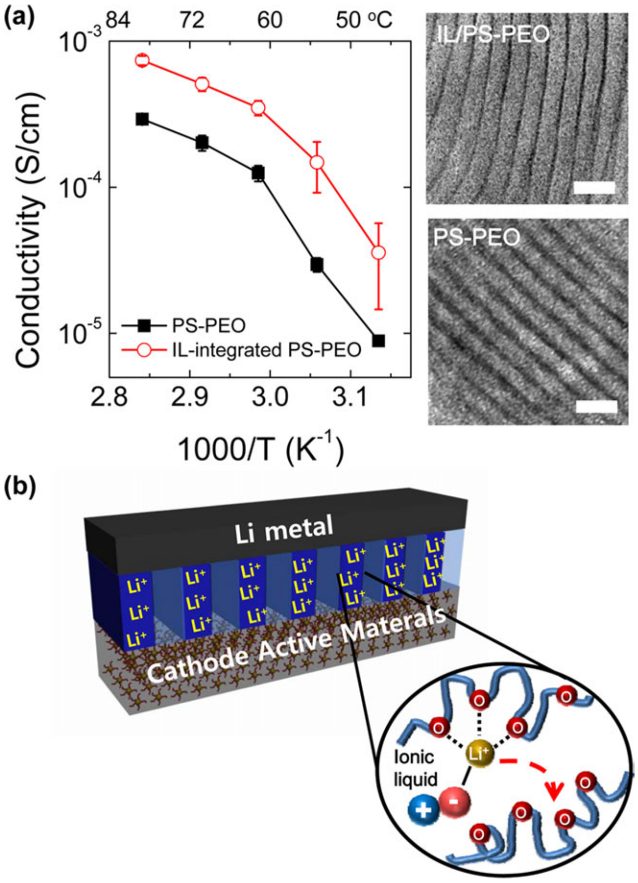


Figure 2. (a) The temperature-dependent ionic conductivity of Li salt-doped PS-PEO block copolymer electrolytes in the presence and absence of ILs. (b) A schematic illustration of Li^+ transport along the IL-incorporated PEO domains of self-assembled lamellar structure. In (a) TEM image of IL-integrated PS-PEO copolymer is shown, compared with that of PS-PEO, where the salt-doped PEO domains were darkened by RuO_4 staining. The scale bars represent 100 nm. Reproduced from Ref. [24] with the permission of American Chemical Society. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Improved Stability of Batteries Using IL-Incorporated Polymer Electrolytes

Given that the solid polymer electrolytes are directed to Li-metal batteries, the compatibility of IL-containing polymer electrolytes with a range of cathode active materials is a matter of concern. Particularly, the replacement of conventional liquid electrolytes by IL-containing polymer electrolytes has been anticipated to reduce the dissolution of cathode active materials into the electrolytes, which has been demonstrated by the significantly improved cycle performance of the battery.[18,79–81] Example of examined cathode active materials includes V_2O_5,[18] $LiMn_2O_4$,[79] $LiFePO_4$,[80] and LiV_3O_8.[81]

The most relevant system associated with the dissolution issue is the lithium-sulfur (Li-S) battery, which has been considered

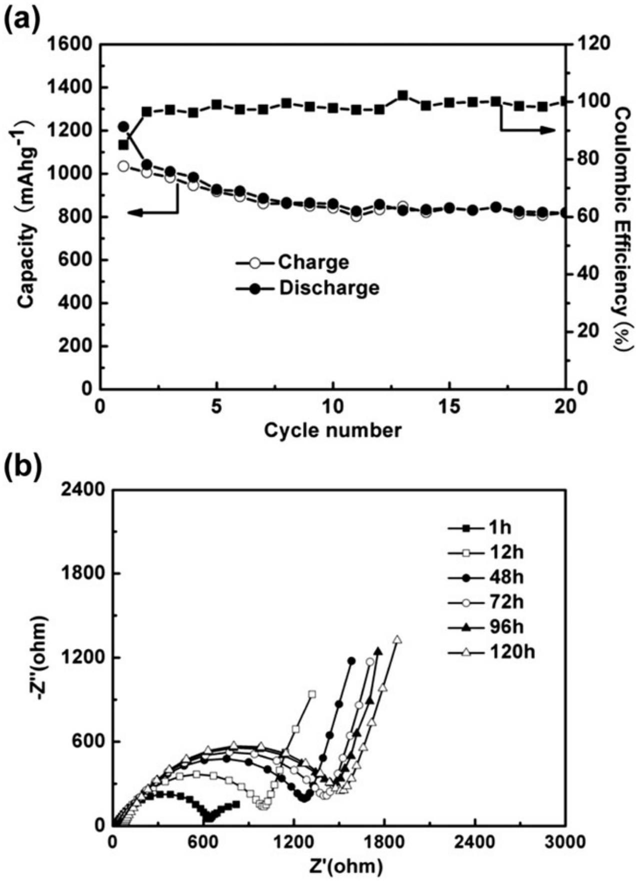


Figure 3. (a) Cycling performance of the Li-S battery comprising IL-incorporated PVdF-HFP against sulfur active materials. (b) Impedance profiles demonstrating the formation of a stable interface between lithium metal and the IL-incorporated PVdF-HFP over 100 hours. Adapted from Ref. [84] with the permission of Elsevier.

as a next-generation lithium battery.[82–86] One of the primary drawbacks of the Li-S cells is the reaction of intermediary polysulfides with conventional liquid electrolytes, which causes irreversible loss of the active sulfur material, resulting in a decrease in the lithium storage capacity after repeated cycling.[84] Consequently, much of the research on Li-S batteries in recent years have been focused on the development of new electrolytes to minimize side reactions.[85,86] Recently, Wu et al.[84] successfully employed IL-incorporated PVdF-HFP in Li-S batteries, which exhibited improved cycle performance against sulfur active materials and good interfacial stability with metallic Li electrode, contrary to the results obtained with liquid electrolytes. Figure 3 shows the cycling performance of the Li-S battery comprising IL-incorporated PVdF-HFP. This implies that the use of the IL-integrated polymer electrolytes could offer promising future avenues for developing next-generation lithium batteries with high capacity, long cycle life, and safety.

Another key factor that is to be considered to achieve improved stability of lithium batteries is obtaining a stable solid electrolyte interphase (SEI) layer. Several studies have identified and characterized the way of forming a stable and reversible SEI layer by using neat ILs that replaced conventional liquid electrolytes. This resulted in synergistically enhanced lithium storage capacities, improved cycling at increased C rates, and high Coulombic efficiencies.[87] Unfortunately, for many IL-incorporated polymer electrolytes, although high ionic conductivities can be achieved, an irreversible formation of the SEI layer was occasionally observed,[88,89] which was responsible for rapid capacity fading during cycling. In particular, for self-assembled block copolymer electrolytes, the formation of the SEI layer resulted in the disruption of the self-assembled morphologies and the blocking of the ion-conduction pathway, eventually leading to the failure of the cells.[24] Therefore, the emphasis of future studies on IL-integrated polymer electrolytes that aim towards their successful application in practical lithium batteries should be placed on the stable formation of the SEI layer.

It should be noted here that a great deal of the recent research efforts have concerned with the use of polymerized ILs as potential solid conductors to alleviate stability concerns.[79,90–92] The blending of polymerized ILs and ILs resulted in an excellent long-term battery cycling performance.[91] One major shortcoming of this approach lies in the relatively lower ionic conductivity of polymerized IL/IL blends in comparison with that of neat ILs. Nevertheless, since the Li^+ transference number in polymerized ILs is largely tunable by adjusting the molecular structure of precursor ILs,[91] the chemical modification of polymerized ILs with Li^+-conducting polymer chains would offer a promising prospect of optimizing the conductivity of electrolytes and stability of batteries.[90]

It is noteworthy that high ionic conductivity, appropriate mechanical stability, thermal stability, and good adhesion characteristics of the polymer electrolytes comprising ILs should make them promising materials for other electrochemical devices such as electrochromic devices,[92] field-effect transistors,[93] and light-emitting electrochemical cells.[94]

Summary and Outlook: Lithium Batteries

The key challenges encountered in the development of IL-incorporated polymer electrolytes to be efficiently utilized in lithium batteries can be summarized as follows. (1) The achievement of high Li^+ conductivity while maintaining high mechanical integrity is of the greatest importance in advancing the battery performance. The types of cations and anions in the ILs, the amounts of ILs incorporated, the morphology of the polymers, and degree of ion-polymer interaction are the factors that affect the conductivity and mechanical properties of IL-integrated polymer electrolytes. Organizing the ion conduction domains of polymers in self-assembled nanostructures is expected to be beneficial in terms of offering a route to increase ion transport rate. (2) The use of IL-incorporated polymer electrolytes is expected to increase the energy density of lithium batteries by allowing the direct use of metallic lithium as an anode. However, it is yet unclear whether these electrolytes will be successfully integrated into next generation batteries. Many aspects, including the dissolution of active materials and the stable formation of SEI layers must be accounted for. It is essential to focus the future studies on the achievement of long term cycling stability against lithium metal at optimized conductivity and elimination of the potential risk of fire.

FUEL CELLS

To achieve high temperature PEMFCs, significant efforts have recently been devoted to the development of new polymer electrolytes with efficient water-retaining properties,[29,95] along with the discovery of new protic solvents that are nonvolatile and have high ionic conductivities to replace water molecules.[31,32] Particularly, ILs comprising heterocyclic diazoles and counterions have recently emerged as promising water substitutes, bearing in mind that the incorporation of ILs into polymer matrices is a facile means of obtaining high conductivity under water-free conditions.[14,96]

It is worthwhile to mention that the thermal stability of many sulfonated polymer membranes have been confirmed to be significantly enhanced with the incorporation of heterocyclic diazoles.[29–31] This signals a great possibility of developing durable fuel cell membranes that can be operated at high operation temperatures. Maximizing the anhydrous conductivity of IL-incorporated polymers has been a significant challenge. The well-established conductivity values of Nafion^{TM} membranes, which are in the range 0.02–0.1 S/cm in the relative humidity range 50–100%, can serve as a benchmark in evaluating the anhydrous transport properties of the IL-integrated polymers. In this section, we discuss the key challenges that are to be overcome to achieve high ion transport rates in IL-integrated membranes by focusing on aspects including the optimization of ILs, mechanical stability of the membranes, and the morphological control towards creating reduced pathways for ion transport.

Factors Governing the Anhydrous Transport Properties of IL-Integrated Polymers

Extensive studies on the IL-incorporated polymer electrolytes reported in the literature have revealed that the transport properties of polymer electrolytes can be significantly enhanced by the addition of ILs upon manipulating the degree of ion dissociation, concentration of ionic moieties, and T_g of the membranes.[36] Nafion^{TM} membranes are most widely examined for their anhydrous transport properties by varying the amounts of ILs and types of ILs.[33,34] The optimized anhydrous conductivity value surpassing 10^{-2} S/cm has been reported for Nafion^{TM} at 180°C upon incorporating imidazolium-based ILs.

As a potential alternative to Nafion^{TM}, polybenzimidazole (PBI) has also received much attention given that IL-incorporated PBI membranes exhibited decent anhydrous conductivity values ranging from 10^{-3} to 10^{-2} S/cm at temperatures above 200°C.[97] Other polymers that have been studied till date are PVdF-HFP,[98] poly(methylmethacrylate) (PMMA) (and PMMA-based copolymers),[39,98–100] poly(2-vinylpyridine) (P2VP) (and P2VP-containing copolymers),[100,101] and poly(styrenesulfonate) (PSS) (and PSS-based copolymers).[14,35,38] The anhydrous conductivity exhibited by the aforementioned polymers was largely deviated, despite the use of the same ILs,[98] implying that the types of polymers play an important role in determining the conductivity of IL-integrated polymers. Table I shows the molecular structures of the most widely employed polymers for the development of IL-incorporated polymers.

Another important factor governing the anhydrous conductivity of IL-incorporated polymers should be the type of ILs, i.e., the cations and anions. In the case of different heterocyclic diazolium cations, the independent variables include the ring structures, number of alkyl substitutions, and the length of alkyl chains. Outstanding transport properties were usually achieved for the ILs comprising imidazole (or alkylimidazole with short alkyl chains), which has been attributed to the efficient ion pairing behavior of imidazole with counter anions to allow for long-ranged ionic association.[14,31,38] The choice of anions also affects the anhydrous conductivity of IL-containing polymers, as systematically investigated for a set of polymers.[14,98,102] The results can be rationalized by a large alteration in thermodynamic properties of IL-integrated polymers including the activation energies for ion conduction[103] and solvation dynamics of ILs,[35] depending on the anions in ILs. Figure 4 represents the effects of cations and anions in the ILs on the conductivity of IL-incorporated polymers.

We hope to comment on the future directions of IL-incorporated polymers. For the practical use of IL-incorporated polymers in PEMFCs, the membranes are required to exhibit high proton transference numbers. In the case of neat ILs comprising Brönstead-type imidazole and [TFSI] anions, the proton transference number was found to range between 0.66 and 0.78.[104] However, many studies have focused on ILs composed of quaternary alkyl imidazole (i.e., aprotic),[33,35,36,105] which are certainly not appropriate for anhydrous high temperature PEMFCs. This is due to the low proton transference number of the PEMs integrated with aprotic ILs despite their high ionic conductivity. This was explored in a recent work of Park et al. who showed that the decreased number of protic sites in alkyl-substituted imidazole leads to the lowering of the ion transport efficiency in IL incorporated PSS-PMB copolymers.[38] In addition, even though the transport properties of a diverse combination of polymers and ILs have been widely examined, the reported conductivity values are yet significantly low in comparison to the values obtained from hydrated membranes. Consequently, it may be highly desirable to concentrate on systems comprising protic ILs to identify the key factors governing the anhydrous ion transport properties in IL-integrated polymers to advance the technology in the near future.

Effects of Morphology on the Anhydrous Conductivity of IL-Incorporated Polymers

There exist diverse observations that substantially improved conductivity values of IL-incorporated polymers can be achieved when the membranes exhibit phase-separated morphologies.[14,33,64,106] This has been a motivation for exploring the morphology-transport relationship for a wide variety of IL-embedded polymers to develop fuel cells with improved performance. However, the limitation of achieving quantitative information on the effects of morphology on conductivity had risen from ill-defined and heterogeneous structures of many IL-integrated polymers studied to date. Significant studies have thus been devoted to the controlled synthesis of new types of polymers having block and/or graft architecture towards the access of well-defined morphologies, taking into account their intrinsic nature to self-assemble.[14,107,108] This enables researchers to establish a synergetic way to obtain optimized transport properties by adjusting the types of ILs, kinds of polymers, and class of self-assembled morphology of the resulting IL-incorporated polymers.

The morphology and transport properties of IL-incorporated PS-P2VP block copolymers have been investigated.[100,101,107] Intriguingly, the nanoscale morphology appeared to change the H-bond structure of the ILs by confinements, which caused increased prevalence of transport by proton hopping rather than by vehicle transport mechanism.[100] This resulted in the lower activation energy for ion transport in self-assembled IL-incorporated PS-P2VP block copolymers in comparison to that in an IL-embedded P2VP homopolymer lacking organization. PS-PMMA block copolymers have also been employed to ascertain the structure-property relationship. Several fold different conductivity values have been observed depending on the types of morphologies and the orientation of the nanoscale domains.[99] These results imply that the morphological designs of IL-incorporated polymers may offer promising future avenues for achieving desired ion transport properties.

While aforementioned studies have successfully demonstrated the effects of self-assembled morphologies on the anhydrous transport properties of IL-incorporated polymers, their application to high temperature PEMFCs seems impractical. This is because PEMFCs require high proton concentrations within the membranes, while protic sites are absent in PS-P2VP and PS-PMMA. In such cases, only ILs can act as proton sources and thus, it is unlikely to realize high proton conductivity. For this reason, many studies have indeed revealed that acid-tethered polymers are yet the most prominent materials that can be used for attaining high anhydrous proton conductivities upon the incorporation of ILs.[109]

Park et al. carried out systematic studies on the morphology and conductivity of IL-incorporated sulfonated polymers by incorporating a range of imidazolium-based ILs.[14,35,38] As a model system, a set of PSS-PMB block copolymers was prepared by varying sulfonation level and molecular weights of the copolymers, in which the PSS phases served as ionic domains for the selective incorporation of ILs. A wide variety of well-defined morphologies such as lamellar (LAM), gyroid, hexagonally perforated lamellar (HPL), and hexagonal cylinder (HEX) phases were observed for the IL-integrated PSS-PMB copolymers.[35,38] Intriguingly, the types of cations and anions in the ILs have been observed to be the most important factors determining the morphologies of IL-incorporated PSS-PMB copolymers, which is attributed to the dissimilar strength of ionic interaction between the ILs and sulfonic acid groups.

Strikingly, at the identical IL loadings, a few orders of magnitude higher conductivities were achieved with the self-assembled IL-incorporated PSS-PMB copolymers, compared to ILs embedded PSS homopolymers.[14] The observation was explained on the basis of the high proximity of ions within the confined PSS domains to build-up less tortuous pathways of ion transport along the PSS domains. It has also been anticipated that the creation of well-arranged ionic channels on nanometer scale may be beneficial in facilitating the ion transport. It is worth mentioning that HPL and gyroid-forming IL-integrated PSS-PMB copolymers appeared to be desirable morphologies to maximize the anhydrous transport properties of IL-incorporated PSS-PMB copolymers. This is closely related to the better connectivity of the ionic channels along the cocontinuous PSS phases in both the structures.[35,38] The results obtained thus far clearly suggest that the structural optimization of IL incorporated polymers cannot be underestimated.

Lastly, the anisotropic orientation of self-assembled microdomains, which is a unique feature of block copolymers, can be readily attained by the application of external fields such as shear flow and electric field.[110] This is expected to result in dissimilar in-plane and through-plane conductivities, which allows for the further enhancement of conductivity along the targeted direction. In the case of IL-incorporated PSS-PMB copolymers, such anisotropy in conductivity has been demonstrated by the use of a simple solvent casting process.[14] LAM-forming IL-incorporated PSS-PMB copolymers specially displayed highly anisotropic in-plane and through-plane conductivities, which differed by 10^4 orders of magnitude. This implies that the alignment approach could be a cost-effective strategy for improving transport properties without changing the chemistry.

Figure 5 summarizes the effects of morphology on anhydrous conductivity described above. The figure (1) compares conductivity values of self-assembled vs. ill-defined morphologies, (2) describes transport efficacy depending on the type of self-assembled morphology, and (3) shows the anisotropic conductivity of aligned samples.

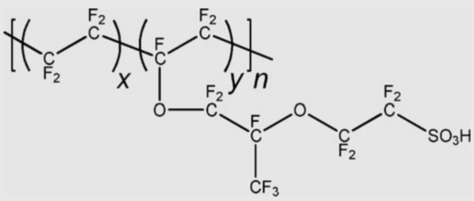
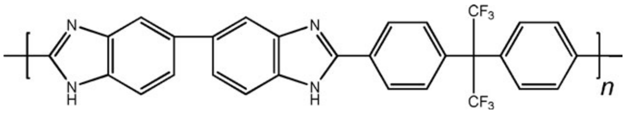
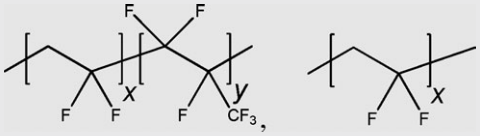
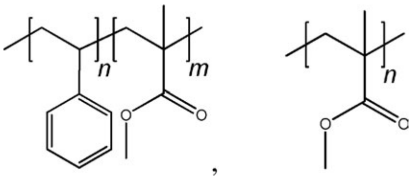
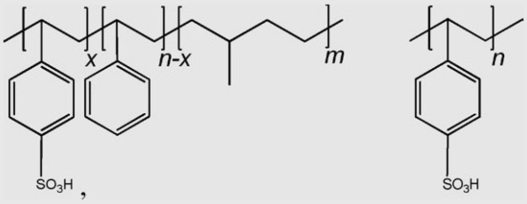
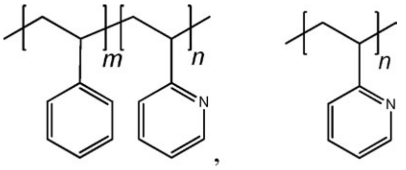
Summary and Outlook: Fuel Cells

In this section, we described the recent advances in the development of new polymer electrolytes that are aimed at applications in fuel cells operating at high temperatures. The findings of the various studies reported in the literature can be summarized as follows. (1) ILs have emerged as promising protic solvents to replace water molecules in fuel cells to enable operation at high temperatures and under anhydrous conditions. A range of IL-incorporated polymers has been tested as next-generation solid-state proton conductors, in which their conductivity has been shown to be largely affected by the types of cations and anions in the ILs, and the kinds of polymers. (2) The creation of nanoscale morphologies in IL-integrated polymers using block-architectures appeared to have a positive influence on improving the conductivity. Depending on the type of the self-assembled morphology, notably dissimilar and high anisotropic conductivity were detected. This suggests that the morphology of IL-incorporated polymers should be taken into account for achieving improved transport properties. (3) Future avenues for the practical use of IL-incorporated polymers in high temperature fuel cells involve the discovery of new protic solvents that result in high proton transference number at low energy penalty for proton conduction. We can expect significant advances in the development of high temperature fuel cells when the aforementioned challenges have been overcome.

ELECTRO-ACTIVE ACTUATORS

Since the strain, response time, and lifetime of actuators can be largely improved with an aid of ILs, the incorporation of ILs into the ionic polymer layer of electro-active actuators has recently attracted immense interest.[111,112] The improvement in

Table I. Molecular Structures of the Most Widely Employed Polymers that Incorporate ILs

Name	Molecular structure	Ref.
Nafion™		33,34
Polybenzimidazole (PBI)		97
Poly(vinylidene fluoride-co-hexafluoropropene) (PVdF-HFP) and PVdF		98
Poly(styrene-b-methylmethacrylate) (PS-PMMA) and PMMA		39,98-100
Poly(styrenesulfonate-b-methylbutylene) (PSS-PMB) and PSS		14,35,38
Poly(styrene-b-2-vinylpyridine) (PS-P2VP) and P2VP		100,101

the performance of the actuators is attributed to the reduced Young's modulus, the facilitated ion transport, and enhanced electrochemical stability of the polymer electrolytes with the incorporation of ILs.[113]

In this section, we will describe two areas that are focused upon whilst developing electro-active actuators comprising IL-incorporated polymers. One involves the effects of ILs on the performance of the electro-active actuators and the other one is with regard to the possibility of developing low-voltage driven actuators by the optimization of ILs and polymers. Further, we will also contemplate the benefits of using phase-separated block copolymer electrolytes in terms of achieving improved actuation performances. On the basis of the discussion on the above mentioned aspects, we will describe the prospects of obtaining future electro-active actuators with low activation voltage and rapid response time.

Effects of ILs on the Performance of Electro-Active Actuators

A major role of the polymer electrolyte layer in actuators is to transfer ions to each electrode under a given electric field. The existence of ILs in polymer electrolytes is anticipated to result

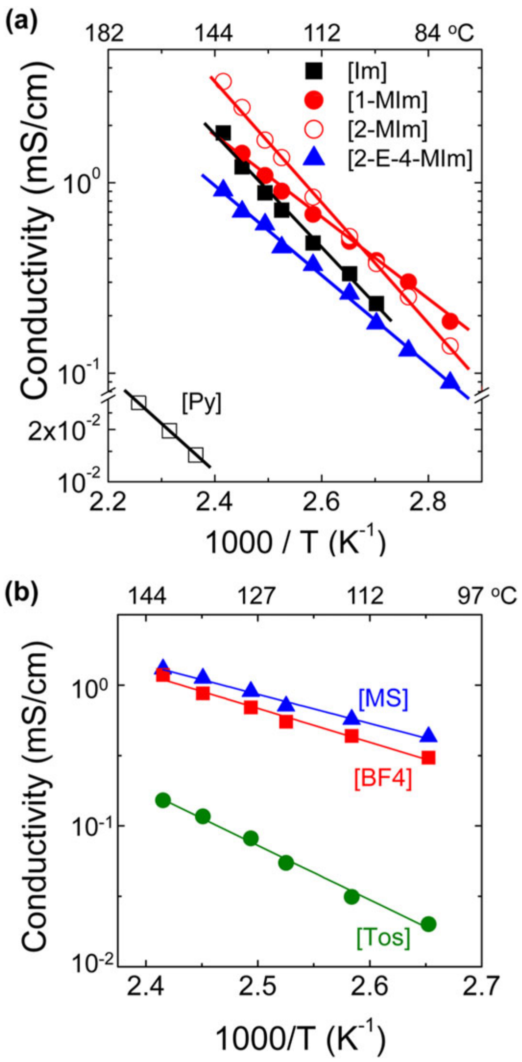


Figure 4. Ionic conductivity of IL-incorporated PSS-PMB copolymers indicating the effects of (a) cations and (b) anions. In (a) and (b), the linear fits were obtained by Arrhenius analysis. The conductivity values were obtained with an equimolar IL concentration and the types of ions are indicated in the figure: [Im]; imidazole, [1-MIm]; 1-methyl imidazole, [2-MIm]; 2-methyl imidazole, [2-E-4-MIm]; 2-ethyl-4-methyl imidazole, [MS]; methane sulfonate, [BF4]; tetrafluoroborate, [Tos]; Tosylate. Adapted from Refs. [38] and [35] with the permission of American Chemical Society. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in large displacements and improved switching speeds of the actuators, in which the factor of prime importance is the types of ILs. To examine the effects of ILs on the performance of the actuators, PVdF-HFP[113–115] and Nafion™[116] have been commonly employed. For example, comprehensive investigation on the effects of the types of ILs on the stress/strain behavior of actuators has been reported by Terasawa et al.[115] using PVdF-HFP copolymers. By employing eight different anions in the ILs, they demonstrated that the actuator containing the larger anion ($[C_2F_5BF_3^-]$) exhibited a higher level of strain than that obtained with a smaller anion ($[BF_4^-]$). This is intimately related to the reduced Young's modulus (and increased viscosity) of the IL-incorporated PVdF-HFP.

It is noteworthy that since the bending mechanism of electro-active actuators originates from charge migration on application of an electric field, the diverse combination of cations and anions in ILs can be expected to enable the direct control of the actuator properties taking into account the different van der Waals volumes of each ion, steric repulsion as a result of charge migration, and the concentration polarization derived from dissimilar diffusivities of the cations and anions.[47] However, given that the ionic conductivity and ion transference number of the IL-incorporated polymers are not always consistent with the values observed in neat ILs due to the confined geometry of actuators,[53,116] the ion transport mechanism in IL-incorporated polymer electrolytes rather than that in neat ILs is to be concretely estimated to improve the actuation performance.

Figure 6 shows the schematic illustration of the bending mechanism of ionic polymer actuators composed of IL-incorporated polymer electrolytes and SWNTs containing ILs. Representative experimental data showing the IL-dependent actuation performance of the ionic polymer actuators are also given.

It should be noted here that when evaluating the actuation performance, one of the important requisites is fast and reliable switching time at a given actuation field. This is primarily associated with the ion mobility (charge migration dynamics) and viscosity (diffusion coefficients) of the ions.[115] One simple means of achieving large displacement and rapid switching speeds of actuators in parallel involves the use of large amounts of ILs within the polymer electrolytes.[117] However, such systems typically exhibit poor mechanical stabilities when subjected to repeated switching signals. This leads us to conclude that the optimization of the type of IL and the amount of IL is essential to achieve efficient and durable electro-active actuators.

Low-Voltage Driven Actuators Obtained from IL-Incorporated Polymers: Novel Electro-Active Actuators Comprising Self-Assembled Block Copolymers

Although extensive studies on ionic polymer actuator have focused on the control of ion migration behavior by adjusting the type of IL, the effects of the type of polymer electrolyte on the actuation performance have received relatively less interest. One common polymer employed is PVdF-HFP[113–115] and an optimized system demonstrates an actuation performance of over 8000 cycles with strains ranging from 0.5 to 2% under 1–3 V. The displacement of the actuators comprising IL-incorporated PVdF-HFP was not found to be linearly proportional to the applied voltage and the decrease in the voltage from 3 to 1 V resulted in 5- to 10-fold smaller displacement.[113]

Since future electro-actuators that are to be applied as bio-inspired systems require low operation potentials (to avoid electric shock from high currents), the actuators developed until now are inapplicable for such applications. In addition, the currently developed actuators have revealed considerably slower switching speeds under small activation fields, which is to be taken in to consideration. This has prompted substantial research efforts towards seeking new polymer electrolytes to achieve fast ion

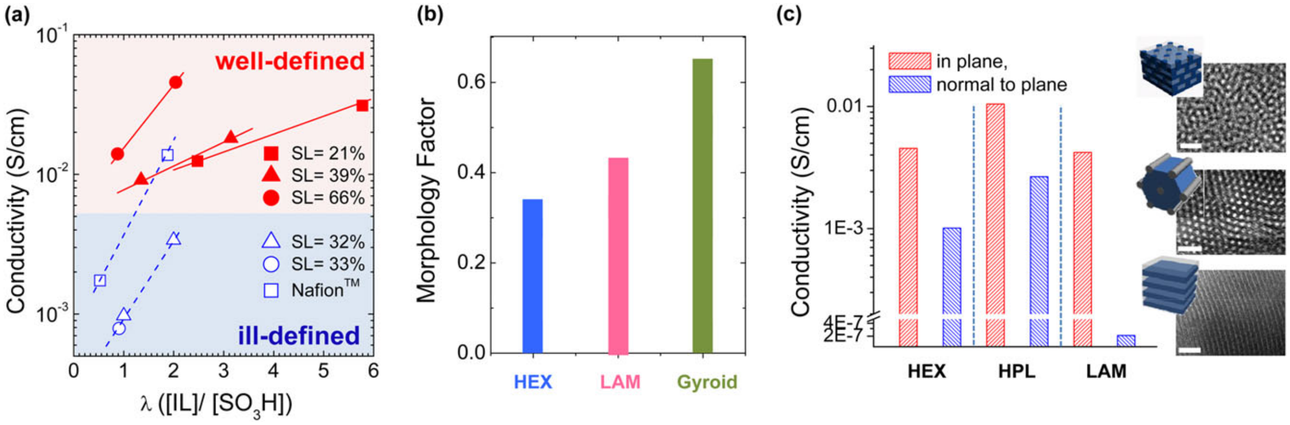


Figure 5. Factors governing the anhydrous conductivity of IL-incorporated PSS-PMB copolymers in connection to morphology effects. (a) The role of phase-separated morphology in enhancing the conductivity, (b) the effects of types of self-assembled morphology on the conductivity, and (c) the dissimilar anisotropic conductivities of solvent-cast membranes depending on the type of the self-assembled morphology. Reproduced from Refs. [14] and [38] with the permission of Nature Publishing Group and American Chemical Society, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transport rates based on rational molecular designs of polymers, accompanied by the alteration of chain architectures.[118,119] This is to optimize polymer relaxation and charge migration synergistically along with optimal mechanical properties.

To explore the role of the type of polymer in determining the actuation performance, the ionic polymer actuators comprising PVdF,[120] PVdF-HFP,[113–115,120] and Nafion™ [116] have been extensively employed. Terasawa et al.[120] made a direct comparison between PVdF and PVdF-HFP and showed that the actuator composed of IL-incorporated PVdF displays much better actuation properties with quick response times than that of actuators comprising IL-integrated PVdF-HFP. The results were explained on the basis of the facilitation of ion motion by the loosely packed chains of PVdF. Liu et al.[121] have also investigated the effects of the type of polymer on the actuation performance by employing a range of polymers including Nafion™, Aquivion™, poly(vinylidene fluoride-chlorotrifluoroethylene) (PVdF-CTFE), and PVdF-CTFE/PMMA blend at a fixed IL concentration. The actuator fabricated using PVdF-CTFE/PMMA blend exhibited the utmost bending performance with the largest strain level, which was demonstrated by the effective electromechanical coupling between the IL and the polymer matrix.

Notably, an additional challenge has recently emerged in developing advanced actuators using block copolymer electrolytes.[122–124] The key to success stemmed from the formation of phase-separated morphologies in IL-embedded polymers to raise the ion transport rate by means of nanometer-sized ionic channels. Particularly, given that the phase-separated nonconducting phases of IL-incorporated polymers can provide effective mechanical support,[14,23,24,38,123] the block copolymer electrolytes can be expected to significantly contribute to the progress in this field.

For example, Watanabe et al.[124] fabricated ionic polymer actuators consisting of PS-PMMA-PS triblock copolymers, in which the PMMA middle block served as the ionic domains for the selective incorporation of ILs. Figure 7(a) shows the representative self-assembled morphology of the IL-incorporated PS-PMMA-PS copolymer. The control of the PMMA volume fractions enabled achieving various kinds of phase-separated morphologies and actuators with different viscoelastic properties. As a result, considerably improved actuation performances were achieved by optimizing the ionic conductivity of the IL-incorporated PS-PMMA-PS, as shown in Figure 7(b), taking advantages of the well-defined ion conduction pathways. The authors also showed the possibility of achieving operation of the actuators at voltages below 1V, although attaining rapid switching times was an issue that remained to be solved.

It should be noted here that while there have been advances in improving the actuation performance with the use of self-assembled block copolymer electrolytes, the achievement of operation at low voltages seems far-fetched. Further investigation on ionic polymer actuators based on rational structural designs is essential for the development of next-generation bio-inspired electro-active actuators.

Summary and Outlook: Electro-Active Actuators

In this section, we described the recent studies on ionic polymer actuators comprising IL-incorporated polymers. From the experimental results obtained from a range of IL-incorporated polymers, the type of ILs, the amount of IL loadings, and the type of polymers appeared to be the key factors affecting the performance of the actuators. The use of self-assembled block copolymer electrolytes seems to be a viable technology to achieve next-generation ionic polymer actuators with fast response times and large displacements that are driven at low voltages. This is because nanostructured polymer electrolytes have a positive impact on the ionic conductivity and ion transference number rather than ill-defined analogues. True electro-active actuators comprising nanostructured polymers are still

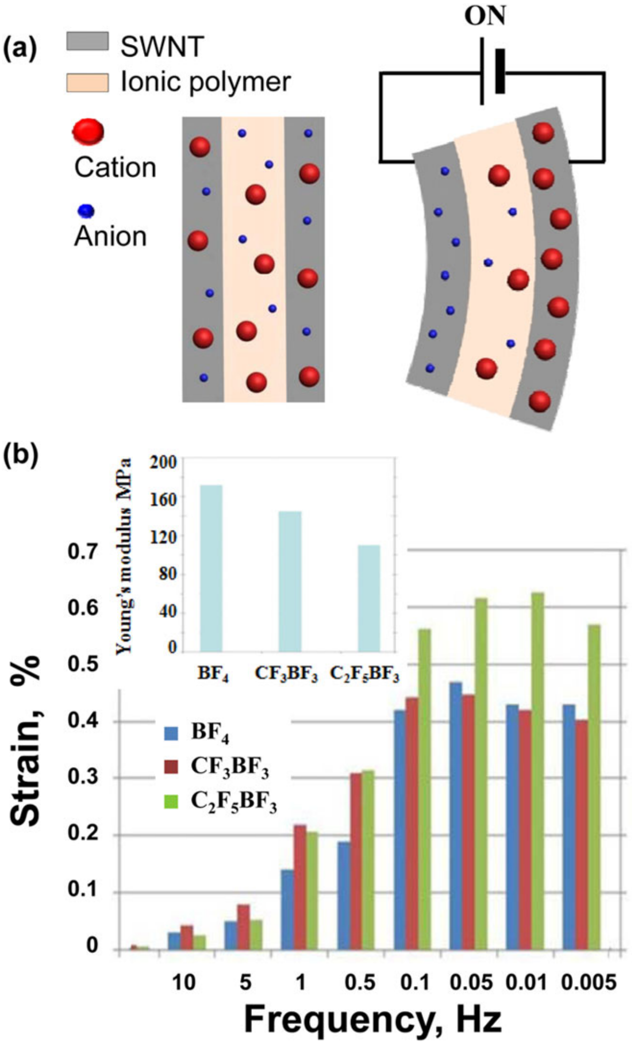


Figure 6. (a) Schematic illustration of the actuation mechanism of actuators comprising IL-integrated polymers and IL-embedded SWNTs. (b) The strain levels of actuators composed of IL-incorporated PVdF-HFP copolymers by varying the types of anions in the ILs. The data were acquired under an operation voltage of 2 V. Figure 6(b) is reproduced from Ref. [115] with the permission of Elsevier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

materials of the future. However, the successful optimization of ion transport properties and mechanical properties of ionic polymer actuators based on polymer electrolytes and ILs with optimal designs can be expected to lead to a breakthrough in the development of electro-active actuators driven at low voltages.

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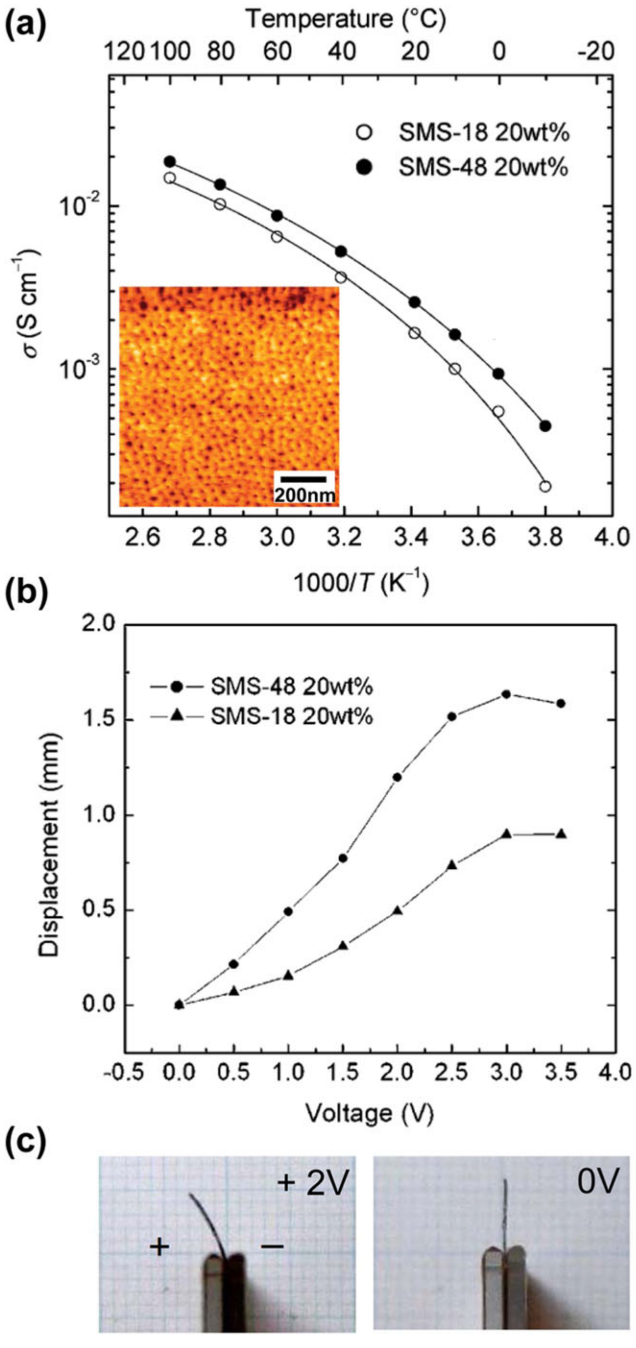

Figure 7. (a) Temperature-dependent ionic conductivity and (b) activation voltage-dependent displacement of ionic actuators comprising IL-containing PS-PMMA-PS triblock copolymers by varying the volume fraction of PMMA blocks. The inset AFM image in (a) shows the representative self-assembled morphology of an IL-containing PS-PMMA-PS copolymer and displacements in (b) were measured at a cycle of 100 s. (c) A photograph of the movement of the actuator with the application of 2V voltage at a cycle of 100 s. Reproduced from Ref. [124] with the permission of American Chemical Society. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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