Design of Superionic Polymer Electrolytes

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Abstract

Despite potential significant advantages of polymer based batteries, the poor ionic conductivity of dry polymer electrolytes at ambient and low temperatures has limited their application. This review describes the approach for improving conductivity by decoupling ionic transport from polymer segmental relaxation. It is emphasized that the decoupling approach is the key for design of superionic polymer electrolytes.

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Introduction

Polymer electrolytes are an important class of solid-state ionic conductors that hold promises for a wide variety of applications in electrochemical devices [1-5,6**,7,8*]. Replacing organic liquid electrolytes with polymer electrolytes would significantly improve safety, reduce weight, and increase energy density for batteries. Nevertheless, the poor ionic conductivity of dry polymer electrolytes at ambient and low temperatures has remained a major obstacle for full exploitation of these materials in vehicle propulsion and other high-power applications.

According to the classical theory, ionic transport in polymers is closely coupled to segmental (structural) dynamics [1,2,6**,9,10] [Fig. 1(a)]. Based on this understanding the main direction of research during the past several decades has been focused on developing polymers with low glass transition temperatures, where fast segmental dynamics would lead to high conductivity. However, it has become increasingly clear that this approach might not be the correct strategy to achieve the desired conductivity level of 10^{-3} S/cm at ambient temperature [11**,12,13**,14*]. It is also possible to speed up the segmental dynamics by plasticizing polymers with some small

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4 molecules. However, this will necessarily compromise some advantages that polymer
5 electrolytes promise to offer.

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7 As a result, a radically different strategy, the decoupling approach, has been proposed
8 [5,11**,12,13**,14*,15*,16,17*,18,19,20*,21-26,29,30*]. The main idea is to decouple the ionic
9 transport from the structural dynamics of the polymer matrix [Fig. 1(b)]. We emphasize that
10 superionic glasses and crystals [31**,32-37], another promising candidate for battery electrolytes,
11 exhibit exceptionally high solid-state conductivity due to their “decoupled” ion conduction
12 mechanism. In that case, the rate of ion jumps is significantly faster than the rate of structural
13 relaxation. However, their intrinsically poor mechanical property (brittleness) makes them
14 unsuitable for many applications. Therefore, realizing superionic conduction in polymers has
15 become one of the “holy grails” in electrolyte science.

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17 Here we present a brief overview of the efforts to achieve superionic conductivity in polymer
18 electrolytes during the last two decades or so, and stresses the new insights from the recent
19 analyses of the relation between ionic transport and structural dynamics in polymers.

20 21 22 **Relation between ionic transport and structural relaxation**

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24 Study of the relation between ionic transport and relaxation phenomenon is a central task in
25 electrolyte science and engineering. To understand and thereby improve the ionic conductivity of
26 polymer electrolytes, one needs to analyze the relation between ionic transport and polymer
27 segmental dynamics. However, after decades of research, the mechanism of ion conduction in
28 polymers is still not fully understood. Moreover, the highest conductivities achieved in solvent-
29 free polymer electrolytes at ambient temperature are still roughly two or three orders of
30 magnitude lower than those of organic liquid electrolytes and conducting ceramics. This
31 difficulty of finding a polymer with sufficient ionic conductivity has raised a fundamental
32 question: are polymer electrolytes intrinsically inferior to other electrolytes in terms of their
33 charge transport capability? The recent analyses [11**,14*,38] of the relation between ionic
34 transport and structural relaxation in polymeric and molecular electrolytes have provided an
35 encouraging and yet surprising answer to this question.

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37 According to the classical theory, the ionic conductivity of an electrolyte solution is determined
38 by the number density (n), ionic mobility (μ_q), and charge (q) of all its ionic constituents (i):

$$\sigma = \sum_i n_i \mu_{q,i} q_i . \quad (1)$$

Among these three factors, the ionic mobility, which can vary many orders of magnitude upon change of temperature, often plays a decisive role. The ionic mobility is related to the diffusivity (D) of the ions through the Einstein relation:

$$\mu_q = \frac{Dq}{k_B T}. \quad (2)$$

Simple consideration of the Stokes law leads to the prediction that the ionic mobility is inversely proportional to the solution viscosity (η) and proportional to the solvent structural relaxation rate (ω_s):

$$\mu_q \propto \omega_s. \quad (3)$$

It has been shown that the Stokes law does not work for many ions in aqueous solutions. Hydrodynamic and microscopic theories have been developed to take into account the effects of dielectric friction [39-41] and ultrafast solvent dynamics [42]. Nevertheless, the proportionality between mobility and structural relaxation rate is still expected to hold to the first approximation. This is supported by temperature-dependent measurements of μ_q and ω_s of molecular electrolyte solutions. The applicability of Eq. 3 to polymer electrolytes is the central point of this review. Experimentally, it is possible to determine both μ_q and ω_s from impedance/dielectric spectroscopy measurement. The ionic mobility can be evaluated from the measured dc conductivity σ using Eq. 1, if the density of “free” ions n_i is known or assumed.

Figure 1. Temperature dependence of segmental relaxation frequency (ω_s) and dc conductivity (σ) for (a) coupled [43] and (b) decoupled polymer electrolytes [13**]. (c) Relation between μ_q and ω_s , Λ and ω_s , for polyethers [14*,43] and the non-polymeric ionic conductors ([11**] and refs. therein). The black line with the slope one is the “ideal” Walden line, representing the case where the conductivity is strongly coupled to structural relaxation. The horizontal dashed line indicates the target μ_q and Λ [11**,14*]. (d) Relation between μ_q and ω_s , Λ and ω_s , for polymers with decoupled ionic conductivity. Samples 1-7 are: 1 - PVC-PPEGMEMA/LiTFSI [11**], 2 - PVEC-PVAc/LiTFSI [11**], 3 - PPEOS_t-PSt/LiClO₄ [11**,13**], 4 - PMOEOMSt/LiClO₄ [11**,13**], 5- liquid-crystalline polymers with LiClO₄ [19], 6 - 0.8(0.5LiPUS-AlCl₃)-0.2LiAlCl₄ [23], and 7 - 90%(50Li-30LiOAc-20LiClO₄)+10%PPO [15*].

A very useful classification of ionic conductors can be made by analyzing the relation between ionic transport and structural relaxation, i.e., performing the so-called (modified) Walden plot analysis [11**,14*,44] [Fig.1 (c), (d)]. To quantify the “intrinsic” conducting capability of ionic materials, their molar conductivities ($\Lambda = \sigma/n_{\text{tot}}$, with n_{tot} being the total number density of ions) or ionic mobilities (μ_q) can be presented as a function of their structural relaxation frequencies (ω_s). A straight line of slope one, passing through a reference dilute salt aqueous solution such as KCl/H₂O and LiClO₄/H₂O, is often called the “ideal” Walden line. It divides the plane into superionic (above) and subionic (below) regimes. “Superior” ionic conductors are those that exhibit ionic mobility (or molar conductivity) much higher than the ideal line. Moreover, the degree of decoupling between conductivity and segmental dynamics can be quantified by using the exponent α from the fractional Stokes-Einstein relation [13**]: $\mu_q = \omega_s^\alpha$ or $\Lambda = \omega_s^\alpha$: the smaller the α , the larger the degree of decoupling. $\alpha = 1$ corresponds to the case of complete coupling, while $\alpha \sim 0$ (e.g. AgI-AgPO₃ glass, Fig.1b) implies completely decoupled ion motions. A few examples of this classification of liquid small-molecule electrolytes and ceramic conductors are given in Fig. 1(c). Three of the small-molecule electrolytes, LiCl/propylene carbonate (PC), LiCl/H₂O, and 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) closely follow the ideal line, indicating strong coupling between ionic transport and structural relaxation, as well as good ion solvation. The inorganic salt, AgI-AgPO₃, stays above the ideal line, exhibiting superionic behavior. The protic ionic conductor, α -picolinium acetate (α -PicAc), appears in the subionic regime because of poor ion dissociation.

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4 It should be noted that the original Walden plot analysis was performed in terms of fluidity ($1/\eta$),
5 instead of structural relaxation frequency (ω_s). This did not allow the Walden plot analysis to be
6 properly applied to polymer electrolytes, because the ionic transport in polymers is controlled by
7 microscopic rather than macroscopic viscosity [11**]. However, it was demonstrated recently
8 that by using structural relaxation frequency, the Walden plot analysis could be successfully
9 extended to polymer electrolytes, yielding new insights about the ionic transport mechanism in
10 polymers [11**,14*,38]. The results of these analyses are summarized below.

11 In the case of polyethers such as PEO and PPG, it is well known that their conductivity is closely
12 coupled to their segmental relaxation. The Walden plot analysis further reveals [11**,14*,38]
13 that the ionic conductivity in polyethers falls surprisingly close to the “ideal” Walden line of
14 aqueous solutions [Fig. 1(c)]. This suggests that the ionic transport (friction) mechanism in
15 polyethers is very similar to those of small-molecule liquid electrolytes. It follows that the
16 relatively low conductivity in polyethers compared with liquid organic electrolytes is mainly a
17 result of their sluggish segmental dynamics. For polyethers to reach the target conductivity of 10^{-3}
18 S/cm, the segmental relaxation frequency has to be $\sim 10^8$ rad/s or higher, even assuming 50 wt%
19 loading of lithium bis(trifluoromethane) sulfonimide (LiTFSI) and its complete dissociation
20 [14*]. In the case of PEO, this is only possible at $\sim 80^\circ\text{C}$ and above. This analysis consolidates
21 the long speculation about the limited performance of polyether-based electrolytes [21]. In other
22 words, it seems impossible for polyether-based electrolyte to reach the required conductivity at
23 ambient and low temperatures, unless the polymer is plasticized.

24 In contrast to polyethers, the ionic transport in other polymers can be strongly decoupled from
25 their segmental dynamics. In general, two types of decoupling behavior have been observed
26 [11**] [Fig. 1(d)]. In materials such as poly[poly(ethylene oxide) styrene]-polystyrene (PPEOSt-
27 PSt) and poly[4-(2-methoxyethoxy)methyl styrene] (PMOEOMSt), ionic conductivity and
28 polymer segmental relaxation exhibit very different temperature dependence, giving rise to
29 prominent fractional Stokes-Einstein behavior. Although these samples fall into the subionic
30 regime at high temperatures due to low free ion concentration (poor ion solvation), the
31 decoupling between conductivity and segmental relaxation brings them in the superionic regime
32 at low temperatures. A different kind of decoupling behavior is observed in polymers such as
33 poly(vinyl carbonate)-*co*-poly[poly(ethylene glycol methyl ether methacrylate)] (PVC-
34 PEGMEMA) and poly(vinyl ethylene carbonate)-*co*-poly(vinyl acetate) (PVEC-PVAc), where
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the relative rates of ionic transport and segmental relaxation are decoupled. These materials show up in the superionic regime at all temperatures.

Different approaches to decoupling

The concept of decoupling of ion conductivity from segmental dynamics has been around for a long time. Already in 1993, Angell and coworkers [15*], using PPG-based electrolytes as an example, proposed the concept of polymer-in-salt electrolytes. In such materials, inorganic salts are the major component and a small amount of polymers serve as a binder or plasticizer. The main idea of the polymer-in-salt electrolytes strategy is to keep the polymer concentration required for good mechanical properties to the minimum, in the hope that the ion conduction mechanism in such highly concentrated electrolytes will approach those of inorganic salts, where relative high and even superionic conductivity is commonly observed.

The pioneering work of Angell and coworkers opened the venue of design of superionic polymers. Ferry, Forsyth, MacFarlane, and coworkers [18,22,45] later extended this polymer-in-salt electrolytes approach to a series of other solid polymers, including poly(acrylonitrile) (PAN), poly(1-vinyl pyrrolidone) (PVP), and poly(*N,N*-dimethyl acrylamide) (PDMAA), and conductivities greater than or equal to 10^{-8} S/cm at the glass transition temperature (T_g) were observed ($\sigma \sim 10^{-15}$ S/cm is expected at T_g in the case of coupled ionic conductivity, see e.g. Fig.1a).

Around the same period, another approach for decoupling conductivity and segmental relaxation in the traditional salt-in-polymer electrolytes emerged from the work of several different groups. The key idea is to frustrate local packing by using rigid polymer structures and thereby increase the free volume and ion mobility. Yamamoto *et al.* [16] reported conductivity of 10^{-6} S/cm at 20°C in rigid poly(parabanic acid) (PPA) with $T_g \sim 350^\circ\text{C}$ and 33 wt% of dissolved LiCF_3SO_3 . Similarly, Wei and Shriver found high conductivities in rigid poly(1,3-dioxolan-2-one-4,5-dioxalate) (PVICOX) [17*]. Based on a slightly different idea, Ingram and coworkers achieved decoupled conductivity in side group liquid crystalline polyethers [19,20*,24]. It was suggested that the bulky pendent side groups in these polymers prevented the ethylene oxide backbones from adopting a close-packed structure. As a result, the conductivities of these polymers were as high as 10^{-6} S/cm at T_g . Recently, this packing frustration approach was also demonstrated by the

Sokolov's group for a few styrene- and carbonate-based polymers [11**,13**,14*], and conductivity comparable to that of the best PEO/LiClO₄ was achieved.

Figure 2. Temperature dependence of ionic conductivity of representative solvent-free polymer electrolytes with decoupled ion transport mechanism. The gray dotted line shows the conductivity of PEO/LiClO₄ (45 wt%) [46] as a benchmark. The open symbols represent polymer-in-salt [15*,17*,18,47] and the filled symbols represent salt-in-polymer [11**,16,19,20*,23]. Samples are: 1 - PVICOX (LiCF₃SO₃, 50 mol%) [17*], 2 - PVIC (LiCF₃SO₃, 50 mol%) [17*], 3 - PAN (LiCF₃SO₃, 45 mol%) [18], 4 - PEC (LiTFSI, 80 wt%) [47], 5 - 90%(50LiI-30LiOAc-20LiClO₄)+10%PPO [15*], 6 - PPA (LiCF₃SO₃, 33 wt%) [16], 7 - MeOC6G6 (LiClO₄, AO:Li=3:1) [19], 8 - 0.8(0.5LiPUS-AlCl₃)-0.2LiAlCl₄ [23], and 9 - PVEC-PVAc (LiTFSI, 50 wt%) [11**]. The horizontal dashed line indicates the target conductivity of 10⁻³ S/cm that is required for many applications [48].

To understand where exactly we stand currently with the decoupling approach, the ionic conductivities of several representative polymer electrolytes are shown as a function of temperature in Fig. 2, together with that of PEO/LiClO₄. In general, relatively high ionic conductivities have been achieved by both the polymer-in-salt and salt-in-polymer approaches. In particular, the conductivity of 0.8(0.5LiPUS-AlCl₃)-0.2LiAlCl₄, the Li-ion conducting polyimide by Zhang *et al.* [23], has reached the required conductivity level of 10⁻³ S/cm at 25°C. The polymer-in-salt electrolyte, PVICOX (LiCF₃SO₃, 50 mol%) [17*], also exhibits high conductivity of ~ 10⁻⁴ S/cm at 25°C. However, it should be pointed out that some of these polymer electrolytes, including 0.8(0.5LiPUS-AlCl₃)-0.2LiAlCl₄ and PVICOX (LiCF₃SO₃, 50 mol%), have not been thoroughly characterized. Further investigation, especially Walden plot analysis, is needed to identify the key elements leading to their apparent success.

To further develop this approach, one needs to understand what controls the decoupling of ion mobility and segmental dynamics in polymers. In the early study by Sasabe and Saito [49], it was proposed that the degree of decoupling correlates with the glass transition temperature of polymers: those with high T_g have a higher degree of decoupling. The subsequent work by Wei and Shriver [17*], Ingram *et al.* [24] suggested that decoupling might originate from polymer packing frustration, but no quantitative analysis was given. The recent work [12,13**] from the Sokolov's group showed that the strength of the decoupling correlates with the fragility but not with T_g . Fragility, defined as $[d\log_{10}\tau/d(T_g/T)]_{T=T_g}$, is a parameter that characterized the steepness of temperature dependence of structural relaxation time τ at T_g . It has been proposed that frustration of local packing structure is responsible for both the decoupling phenomenon and the increase in fragility. Therefore, it should be possible to synthesize polymers with relatively low T_g , while maintaining the decoupling properties through strong frustration in packing.

Conclusions and outlook

In this article, we have briefly reviewed the decoupling approach to solid polymer electrolytes and the new insights provided by the analysis of the relationship between ionic transport and polymer segmental relaxation.

The presented results and analysis indicate that:

- There is a fundamental difference between the ionic transport mechanisms in polymers and small molecules. The ionic conductivity in polymers can be strongly decoupled from

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4 their segmental dynamics, in terms of both temperature dependence and relative transport
5 rate.
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8 ➤ Decoupling conductivity from segmental relaxation is the key for design of superionic
9 polymers. Many polymers show the desirable characteristics similar to superionic
10 conductors. A clear understanding of how to enhance these features is critical to the
11 successful design of solid polymer electrolytes.
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13 ➤ Lastly, while many polymer electrolytes should be considered as superionic in terms of
14 the intrinsic relation between transport and structural relaxation, their sluggish segmental
15 dynamics and mediocre ion solvation are responsible for the low ionic conductivity at
16 ambient and low temperatures.
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22 We hope our view could serve as a basic guideline for development of superionic polymer
23 electrolytes. Going forward, several critical issues still need to be addressed. First, while the
24 general connection between polymer packing frustration and decoupling has been observed, the
25 detailed link between chemical structure and ionic transport mechanism is yet to be established.
26 Second, the analysis of the relation between conductivity and structural relaxation has been so
27 far limited to the case of salt-in-polymer electrolytes. As the salt concentration increases, a
28 crossover from segmental dynamics facilitated conduction to vacancy dominated hopping
29 conduction characteristic of solids should be expected. To obtain a complete understanding of
30 the relation between charge transport and relaxation in polymer electrolytes, it is necessary to
31 extend the analysis to polymer-in-salt electrolytes. Lastly, high ionic mobility must be combined
32 with high free-ion concentration to achieve high ionic conductivity. How to identify polymer
33 structures that promote both decoupling and ion solvation remains a challenge.
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44 While this review is focused on the traditional polymer-salt mixtures, the decoupling approach is
45 also critical to the design of other types of polymer electrolytes including polymeric single-ion
46 lithium conductors and polymerized ionic liquids. They have significant advantage due to high
47 transference number, i.e. exclusive motion of the desired ion (e.g. Li) while the counter-ion is
48 attached to the polymer chain. In contrast to closely coupled transport mechanism in regular
49 aprotic ionic liquids, strong decoupling of ionic conductivity from segmental relaxation has
50 already been observed in many polymerized ionic liquids [50,51*]. A thorough investigation of
51 the relation between ionic transport and segmental dynamics in these novel materials may
52 provide the opportunity to further improve their properties.
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