Multivalent Ion Conduction in Solid Polymer Systems

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High energy density energy storage devices are required to advance consumer electronics, electrified vehicles, and grid storage for renewable energy generation. Multivalent batteries, such as those based on Mg^{2+}, Zn^{2+} or Al^{3+}, improve volumetric energy density, reduce cost and enhance device safety over lithium-ion batteries. However, advances are required to develop electrolytes that enable stable cycling for rechargeable systems. Polymer electrolytes present enhanced mechanical and electrochemical stability over organic liquids, which could facilitate the expansion of rechargeable multivalent battery technology. This perspective highlights current research on multivalent polymer electrolytes and discusses the challenges for improving ionic conductivity in these systems. We identify a need for improved systematic study of promising polymer candidates. Molecular design strategies should focus on enhancing ion dissociation and mobility. Dissociation can be tuned using highly polarizable species within the polymer backbone or pendant groups to improve the polymer dielectric constant. Cation mobility is increased when polymer solvating groups interact weakly with cationic species. This can be achieved either through bulky, labile coordinating moieties, or through the design of single-ion conductors with immobile anions.

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Multivalent Ion Conduction in Solid Polymer Systems

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While polymer electrolytes hold the promise of improving safety and mechanical durability of electrochemical devices, most suffer from relatively low ionic conductivities especially at ambient temperature. Furthermore, much of the conductivity in polymer electrolytes stems from the mobile anions, rather than the metal cations necessary for energy storage. This combination of challenges becomes even more pronounced in the conduction of the multivalent metal ions likely to be necessary for next generation, high energy density energy storage devices where the ions are likely to have complex, multi-functional interactions with the polyelectrolyte matrix. Herein, we will review the current state of understanding of the mechanisms of multivalent ion transport through polymers and the specific challenges relative to lithium ion transport. This fundamental understanding will lead to the design of new polymer electrolytes for multivalent ion transport, including single-ion conductors and anion-trapping polymers for enhanced cation mobility.

Introduction

The development of lithium ion battery technology has enabled rapid advances in consumer electronics while providing promise for applications such as grid storage and electrified transportation. While lithium boasts high gravimetric energy densities and the lowest reduction potential, safety concerns motivate the development of new chemistry platforms. Multivalent batteries, such as those based on Mg^{2+}, Zn^{2+} or Al^{3+} can dramatically reduce cost and improve device safety due to their increased abundance and reduced reactivity.[1-4] Further, multivalent batteries have higher volumetric energy density compared to lithium.[1] While metallic lithium anode batteries can obtain theoretic volumetric energy densities of 2062 mAh cm^{-3}, this is increased to 3833 mAh cm^{-3} for magnesium and 5851 mAh cm^{-3} for zinc.[1] This results from the larger charge to ionic radius ratio for many multivalent cations compared to Li^+. However, many challenges exist for multivalent battery chemistries, most importantly the low mobility of multivalent ions in both electrode and electrolyte materials due to the higher charge density of multivalent species leading to stronger interactions with the surrounding matrix.[5] Further, electrochemical compatibility presents a significant challenge because of the lack of understanding of how a solid-electrolyte interphase (SEI) would function in these materials. This is particularly true in magnesium batteries where stable Mg^{2+} stripping and plating is mostly limited to liquid electrolytes such as those based on Grignard reagents or oligoethers.[6-7]

The enhanced mechanical and electrochemical stability of polymer electrolytes compared to organic liquids makes them advantageous for both lithium-ion and multivalent ion batteries. Their mechanical robustness facilitates device processability while maintaining intimate contact with electrodes during battery cycling. Polymers can also function as both the electrolyte and separator material, potentially enabling higher energy density devices.[8] Further, the thermal and electrochemical stability of polymers enhances overall device safety and widens the operating voltage window, allowing for a broader range of cathode and anode chemistries[9] such as enabling reversible stripping and plating of magnesium metal anodes.[6] However, similar to the case of lithium transporting polyelectrolytes, multivalent ion transporting polyelectrolytes exhibit low ionic conductivities which limits their practicality for applications. While adequate conductivities of 10^{-3} S cm^{-1} are sometimes achievable at elevated temperatures, room temperature conductivities are generally at least an order of magnitude lower.[10] This deficit is exacerbated for most polymer electrolytes because these conductivities reflect total ion motion while only cations contribute to the battery function.[11-12] The actual cation conductivity is usually a minority fraction of the total quoted ionic conductivity (transference numbers <<1). High anion mobility also creates concentration gradients that may lead to uneven metal plating and stripping.[13]

Increased understanding of the mechanisms of ion transport in polymers can provide guidance for the design of polyelectrolytes optimized for multivalent ion transport. Ionic conductivity is broadly governed by two interconnected factors: ion concentration and ion mobility.[14] Optimizing the electrolyte requires a detailed understanding of how the polymer environment affects the structure and mobility of the dissolved salts. Ion concentration is linked to the extent of salt dissociation, which depends on the identity and concentration

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x of the cation and anion as well as the interactions between the ions and the polymer matrix. Typical ion conducting polymers have dielectric constants an order of magnitude lower than comparable liquid electrolytes, significantly reducing ion dissociation and increasing the importance of ion identity. The connectivity and chain architecture of polymers has been shown to affect the local dielectric environment around solvated ions, leading to further behavioral differences between polymers and liquid electrolytes.[15-16] The use of more polarizable or larger counterions with smaller lattice energies should lead to higher dissociation rates and improved ionic conductivity.[17] Further, while increasing salt concentration should increase ion concentration, ion-ion interactions result in the formation of ion pairs or larger aggregates which reduce the ion concentration from its theoretical maximum value. These ion-ion interactions also reduce the mobility of ions due to coulombic drag forces and dynamic polymer crosslinking.[8] Experimental and theoretical studies suggest that increasing the dielectric constant of the polymer environment can reduce ion-ion interactions by improving screening between ion pairs, thus leading to enhanced dissociation and ion mobility.[18-19]

Ion-polymer interactions also play a significant role in ion mobility. Polymer solvation sites, which stabilize the dissociation of a salt into its respective ions, generally interact more strongly with cationic species, which are also the ions of interest for most applications. Polymer segmental dynamics, generally tracked by the polymer glass transition temperature, T_g, affect the mobility of ions and are commonly accounted for through a Vogel-Fulcher-Tamman (VFT) relationship of conductivity with temperature. The dynamics of the polymer-cation solvation interaction also govern ion mobility by determining the timescale for release of the cation species from relatively immobile solvation sites.[20]

Since a majority of published work on lithium-ion conducting electrolytes relates to Li^+ in poly(ethylene oxide) (PEO) derivatives, the overall scope of design rules established is conflated to some degree with the specific attributes of PEO's interaction with Li^+. Recent work suggests that other polymer chemistries interact differently both with Li^+ and other battery-relevant ions.[21-23] For example, while ion-ion interactions still dominate performance, the effect of the T_g appears to be less important in governing ion mobility in non-polyether chemistries.

In this perspective, we summarize efforts towards understanding the mechanisms of multivalent ion transport in polymer electrolytes and the challenges and opportunities associated with the introduction of multifunctional, multivalent ions into polymer systems. This discussion is divided into four sections; we begin with an overview of the parameters governing ion conduction in polymer electrolytes, focusing on experimental measurement techniques and common pitfalls. We then provide an overview of the synthetic progress in multivalent polymer electrolyte design and the resulting trends in ionic conductivity and ion aggregation. Further, we discuss the complex interactions between multivalent ions and a polymer matrix, which create both challenges and opportunities in tuning the polymer mechanical properties separately from ionic conductivity. Finally, we include an outlook on future research directions, including the importance of performing more systematic studies and examining new synthetic systems based on anion traps or single-ion cation conductors.

I. Measuring ion transport properties

Improving ionic conductivity in mono- and multivalent polymer electrolytes requires increasing ion concentration and mobility. High ion concentration is achieved through the long-lived dissociation of a salt into its respective ions, without aggregation into pairs, triplets or other species which could impede ion motion. Spontaneous dissolution of salt into a polymer requires a negative Gibbs free energy, which results from a more negative solvation energy of the ions within the polymer compared to the lattice energy of the salt. Typically, cations rather than anions are solvated by the polymer, and thus interact more strongly with the polymer matrix. Since these are also the species of interest for conduction, there is an inherent trade-off between salt dissolution and subsequent cation mobility. Microscopically, ion mobility is achieved through successive ion hops from a current solvation site to a nearby open site.[8, 24-25] The probability of a successful hop hinges on the proximity of a nearby open site and is mediated by local fluctuations in distance between sites (Figure 1). Thus, for polymers above their T_g, the motion of ions is generally related to the segmental dynamics of the polymer.[20, 26] Anion mobility is also loosely tied to the glass transition temperature, as anions require free volume or segmental rearrangement to move through the polymer matrix. The goal is to use salts with as low a lattice energy as possible for maximum dissociation and to design a polymer with labile cation interactions, or preferential anion interactions, to enhance cation mobility. For multivalent species, these requirements become more challenging, since charge densities increase, resulting in larger salt lattice energy and stronger polymer-ion interactions. Thus, multivalent cations are expected to exhibit more ion pairing and aggregation as well as lower mobilities.

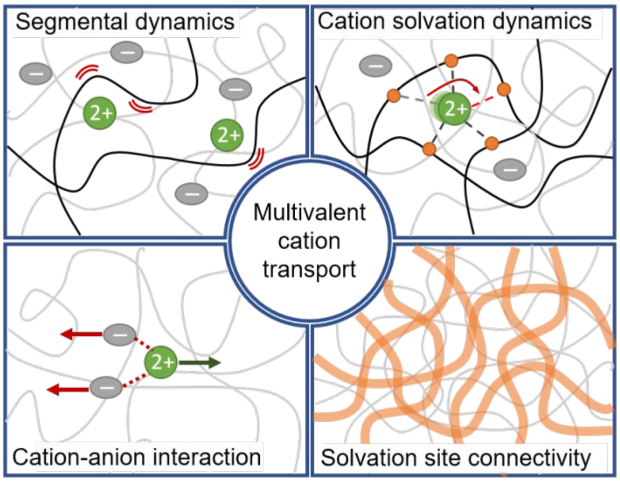

Figure 1. Overview of factors affecting the performance of multivalent ion transport in polymer electrolytes. These include the importance of segmental dynamics, the timescale for solvation site exchange, cation-anion interactions, and solvation site connectivity (*i.e.*, percolation shown in orange) in determining ion mobility and the fraction of current transported by the cation of interest.

In addition to bulk ionic conductivity, the contribution from the ion of interest, typically the cation species, is extremely important for applications. This metric is known as the transference number, and is defined most broadly as

$$t_+ = \frac{\sigma_+}{\sigma_{total}}$$

where σ_+ is the contribution to the conductivity from the cation, and σ_{total} is the total ionic conductivity. The product of the cation transference number, t_+, and the total conductivity, σ_{total}, thus provides a measure of the cation conductivity.[27] A more precise definition of transference number depends on the method used for measurement.

Transference number measurement is not straightforward in polymer electrolytes, with significant discussion arising over the past few decades on the appropriate experimental techniques to accurately capture the transport behavior of the cation. Electrochemical impedance spectroscopy (EIS), typically used for ionic conductivity measurements, is an ac current technique and does not distinguish the species which contribute to the measured total ionic conductivity, although several methods have been proposed for extracting transference numbers. It is important to note that drawbacks for each of these methods arise in the case of lithium-ion conducting polymers[28-30] and seem to be exacerbated for multivalent ions due to their higher propensity to form ion aggregates, as well as their generally higher interfacial resistances with non-blocking electrodes of their corresponding metals.

Chronoamperometry is the simplest and most common way of measuring transference number but becomes inaccurate in systems with high interfacial impedance or with ion pairing.[31] In this method, a constant voltage is applied to a symmetric cell with non-blocking electrodes for the ion of interest, and the current is tracked as a function of time until steady-state is reached. The transference number is then calculated as

$$t_{+,ss} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$

where ΔV is the potential difference applied across the cell, I is the current and R is the interfacial resistance, and the subscript *ss* corresponds to measurements performed at steady-state while *0* corresponds to measurements at the beginning of the experiment prior to polarization.

This method has been used to report transference numbers for a variety of multivalent polymer electrolytes, with widely varying results. For Cu^{2+} in poly(ethylene oxide) (PEO), values range from 0.08[32] to 0.24.[33] Labile divalent species such as Hg^{2+} and Pb^{2+} exhibit high transference numbers of 0.25 and 0.6, respectively.[34] It was suggested that the known lability of Cu^{2+} and Hg^{2+} for metal-ligand water exchange rates correlates well with measures of higher contribution to the current from the cation species in PEO.[35] Transference numbers for Mg^{2+} with ClO_4^- counterions in PVA/PAN blends, are measured to be reasonably high, ranging from 0.27 to 0.33 even though Mg^{2+} is expected to have slow exchange rates as measured in aqueous solution.[36] It is possible that the addition of solvating groups distinct from ether oxygens, as well as the use of different anion species could be enhancing the cation transport in these systems; however, these values should be regarded with caution until a more systematic study is performed due to some challenges in implementing such measurements. First, the quoted transference number is highly dependent on the initial current reading, I_0, with a slower data acquisition speed resulting in a lower initial current and thus an improved transference number. This was recently addressed for lithium electrolytes, with the suggestion that the initial current be calculated from the initial impedance rather than the first recorded point in the chronoamperometry.[28] Further, to get enough current signal for accurate measurement, large cell polarizations are needed. This stems from the inherently low conductivity of polymer electrolytes as well as the large interfacial resistances commonly observed in symmetric cells containing multivalent metals. Strictly speaking, the theory mentioned above only holds for small potentials on the order of 10 mV, though many studies use 20 mV or even 100 mV for measurement without significant issue; applied voltages up to 1 V, however, are a significant departure from equilibrium and are too large for accurate application of this theory. Large changes of interfacial resistance over the course of the measurement also present a concern, as this suggests significant parasitic reactions and decomposition that could be contributing to the measured current.[37] Lastly, the issue of ion pairing affecting the transference number measurement cannot be overlooked; in concentrated or otherwise non-ideal electrolytes where ion-ion interactions are most prevalent, the above relationship does not hold, and a more detailed understanding of the mobility of various species is needed for transference number analysis.[38-39] This is especially relevant for multivalent electrolytes, which tend to have stronger ion-ion interactions, as discussed further below. Given the above complications with this technique, it is not surprising that transference number measurements for multivalent ions vary widely. At the very least these experiments suggest that divalent ions are indeed somewhat mobile in polymer electrolytes.

Nuclear magnetic resonance (NMR), specifically pulsed-field-gradient (PFG) NMR, has been used as an alternative strategy for measuring diffusion coefficients of ions of interest which can then be used to calculate transference numbers. PFG NMR measures the diffusion coefficient of an NMR active nuclei, with the ability to both distinguish ion environments through chemical shift and measure multiple diffusion coefficients of nuclei within the same chemical shift environment.[40-41] However, for many polymer systems, this technique cannot distinguish between the motion of unassociated single cations and those aggregated with other ions because PFG NMR measures diffusion over a length scale of a few micrometers. Ions hop through a polymer matrix in a series of association and dissociation events with both solvating units on the polymer and with their counterions. Over the time and length scale of a PFG NMR measurement, the ions being tracked have existed in a mix of environments ranging from mobile ions to immobile solvated ions to aggregates. The diffusion coefficient measured is thus an average diffusion coefficient weighted by the time spent in the various mobile and immobile environments. This exchange between environments over the PFG NMR measurement timescale makes it more difficult to identify the exact nature of the mobile nucleus of interest. However, it does allow for determination of whether the species is mobile at all. A PFG NMR transference number is defined, for a multivalent cation with monovalent anion salt, as

$$t_{+,NMR} = \frac{z_+ D_+}{z_+ D_+ + D_-}$$

where z_+ is the valency of the cation, and $D_{+/-}$ are the diffusion coefficients of the species containing the cation and anion as measured via PFG NMR. Thus, this measurement of transference includes the implicit assumption that all ions are perfectly dissociated and non-interacting over the course of the measurement. A promising opportunity to begin to extract the diffusion coefficient of solely ionic species within polymer systems comes with electrophoretic PFG NMR, which measures the diffusion under an applied electric field and thus weights the diffusion of ionic species more heavily.[42-43] This technique is not readily available, however, and has yet to be applied to polymer electrolytes.

While gaining prevalence in lithium-based conductors, PFG NMR has only been used in one instance for multivalent ion conductors due to the difficulty of finding appropriate multivalent nuclei for NMR.[44] While many divalent species are NMR-active, most have such low gyromagnetic ratios or abundance that direct detection, especially for diffusion measurements, is infeasible. This necessitates indirect confirmation of mobility through a comparison between the total ionic conductivity measured by EIS and that calculated from diffusion coefficients measured via NMR. The ionic conductivity contribution that is expected from a set of *i* species based on their diffusion coefficients can be calculated as

$$\sigma = \frac{F^2}{RT} \sum z_i^2 c_i D_i$$

where *F* is Faraday's constant, *R* is the ideal gas constant, *T* is the absolute temperature, and z_i, c_i, and D_i are the valency, concentration, and diffusion coefficient of the i^{th} species.[14] This equation requires knowledge of the exact concentration of ions present as well as their diffusion coefficient; typically, it is assumed that the salt is fully dissociated and thus the relevant ion concentration is the initial concentration of salt added to the system. This assumption provides an upper bound on a species' conductivity contribution. If the conductivity contribution from the measured species is insufficient to recover the total ionic conductivity measured via EIS, then an additional species must be present in the system to contribute the remaining conductivity. This technique was used in recent work on Zn^{2+} conductivity within a PEO-imidazole polymer system.[44] The anion diffusion coefficient was measured using PFG NMR, and the ionic conductivity was calculated assuming no cation contribution. It was found that this conductivity underestimated that which was measured using EIS, indirectly suggesting a contribution from the Zn^{2+} cations within the system. Importantly, it should be noted that while the mobility of the divalent Zn^{2+} species was estimated to be slightly less than half of the corresponding Li^+ species in the equivalent polymer system, the contribution to the conductivity was comparable between the two ions ($t_+ = 0.18$ for Li^+ and $t_+ = 0.13$ for Zn^{2+}). This highlights the benefit of a multivalent as opposed to monovalent cation for conductivity: assuming the same cation concentration, a multivalent cation can have a diffusion coefficient that is smaller by a factor of its valency and still contribute equivalently to the ionic conductivity. Indirect measurements of transference number using PFG NMR do not work for all multivalent cations. For some multivalent species such as Cu^{2+}, unpaired electrons significantly increase the speed of NMR signal decay, making diffusion measurements of even the anion species impossible under most experimental conditions. Thus, this technique will be limited to either NMR-active nuclei, or at least NMR-friendly nuclei for indirect measurements of cation contributions to ionic conductivity.

A more rigorous method for transference number determination stems from thermodynamic considerations but is limited by experimental complexity and propensity for propagating error.[39] The transference number can be calculated from separate measurements of potential versus concentration, restricted diffusion, and steady-state current. Unlike the previous two techniques, this method holds for concentrated and non-ideal solutions.[39] These measurements require non-blocking electrodes (e.g. metal foil) for the metal cation of interest and have been shown to result in negative transference numbers as low as –0.38 and –4.4 for Li^+ and Na^+, respectively, in PEO.[28, 39] This is in stark contrast to measurements using the steady-state or PFG NMR methods on the same systems, where the transference number remained positive over the entire concentration range. The existence of ionic clusters can give rise to negative transference numbers, which means that current is primarily transported by negatively-charged aggregates, and thus cations move in the "wrong" direction within a cell.[28, 39] Unfortunately, this method is not popular, possibly due to the number of experiments that must be performed. One potential issue for these measurements is that they can be influenced by the presence of a solid electrolyte interphase (SEI) that typically forms between the polymer and metal foil. This shortcoming has been acknowledged for lithium systems and could play a significant role for multivalent systems if a stable interface cannot be formed, or if the interfacial resistance becomes too large.[28] To our knowledge, this method has not yet been applied to multivalent electrolytes. Nonetheless, the use of this technique for multivalent electrolytes could provide critical information about the primary means of cation transport in such systems.

II. Synthetic design of multivalent conducting polymer electrolytes

Targeted synthetic design of high conductivity polymers requires identifying the most important design features. Possible important factors include the anion identity, the solvation site chemistry, and the polymer T_g in affecting free ion concentration and ion mobility. Due to the larger volume of studies performed on Li^+ conductors, much of what we have learned about synthetic design of polymer electrolytes stems from monovalent conductors; most of this knowledge is expected to transfer reasonably well to the multivalent systems, though changes polymer-cation interactions can lead to additional complicating effects especially with solvation chemistry. Figure 2 and Table 1 depict the range of polymer chemistries and salts studied for multivalent ion conduction.

While solvents and plasticizers can be added to polymer electrolytes to depress T_g or enhance ion dissociation, the addition of mobile small molecules introduces stability concerns and alters the mechanism of ion transport.[45-48] Ion conduction within such gel electrolytes is dominated by vehicular transport of solvent molecules rather than direct interaction with the polymer. Herein we focus on *dry* solid multivalent ion conducting polymers, where conduction mechanisms are directly tied to interactions between the ions and polymer host. Importantly, while such systems should be solvent-free during operation, the effect of the solvent used for mixing and casting polymer electrolytes is often overlooked. Though all the studies mentioned within include vacuum drying steps to remove excess solvent, the success of removal is not always quantified and can have significant implications for ion mobility and conductivity.[49-50] This points toward an underlying cause for the sometimes widely varying conductivity results reported for some multivalent conducting polymers and highlights the importance of a continued effort for precise control of preparation and measurement conditions.

Multivalent salts mixed in PEO typically show reduced ionic conductivity compared to their monovalent counterparts (Figure 3). The crown-ether-like solvation of cations by the ether backbone of PEO creates stable cation complexes, which can enhance salt solubility but also limit cation mobility. Incorporation of multivalent halide salts of Hg^{2+} and Cd^{2+} in PEO slightly predates alkali metal-PEO complexes;[51-52] however, initial mention of ionic conductivity in PEO starts with alkali metals in the early 1970s,[53] with studies of multivalent ion conduction appearing later in 1986.[54-55] Room temperature conductivities of multivalent salts such as $MgCl_2$ and $Mg(ClO_4)_2$ in PEO ranged from 10^{-8} to 10^{-6} S cm^{-1}, respectively, and at elevated temperatures reached values comparable to $LiCF_3SO_3$ PEO electrolytes. Ionic conductivity with other cations is generally lower, around 10^{-7} and 10^{-8} S cm^{-1} at 30 °C for $Zn(ClO_4)_2$ and $Ca(ClO_4)_2$, respectively.[54] As work on multivalent conductors expanded, the conductivity and transference numbers reported for such electrolytes varied widely.[50] This variability in performance likely stems from changes in processing conditions, such as the solvent used for casting, as well as anion identity and quality of measurements.[50] Further variances can stem from differing crystallinity of the PEO-salt systems at temperatures below about 60 °C. Crystalline domains generally exhibit lower conductivity, and a lack of characterization of the extent of crystallinity hinders a true comparison of electrolyte performance. For example, the addition of 35 wt% $Cu(CF_3SO_3)_2$ into PEO resulted in a room temperature conductivity of 4×10^{-5} S cm^{-1},[32] which is over an order of magnitude higher than that of $LiCF_3SO_3$ due to the slow phase re-equilibration during cooling that suppresses PEO crystallization for the Cu^{2+} salt.[33] Above the melting temperature of PEO the Li^+ salt regains performance, with twice the conductivity as the Cu^{2+} equivalent. The ionic conductivity of Mg^{2+}, Ca^{2+} and Zn^{2+} with $CF_3SO_3^-$ anions in PPO is reasonably similar across the series at low temperature (10^{-7} S cm^{-1}), though at 95 °C the $Zn(CF_3SO_3)_2$ salt is almost an order of magnitude more conductive than the Mg^{2+} equivalent (Figure 4).[56] This is correlated with the extent of ion dissociation, as will be discussed presently.[56] Similar to Li^+-PEO systems, the ionic conductivity seems to increase with large and easily polarizable anions which lower the lattice energy of the salts and enhance dissociation.[17] However, the mobility of multivalent ions depends dramatically on the presence of water or residual solvent as was shown for Ni^{2+}-PEO electrolytes; thus care must be taken from the outset to mitigate water uptake and use low boiling point solvents.[49-50]

A benefit of PEO which enhances ionic conductivity for Li-ion systems compared to other polyethers is the highly percolated network of nearby solvation sites for the ion to move into.[57] It is likely that solvation site connectivity also plays a large role for multivalent conduction and is an important but challenging factor to consider for new polymer electrolyte design. Still, constraining electrolyte design to ether-based solvating sites may be limiting electrolyte ionic conductivity, especially for multivalent species which show extremely stable complexing with crown ether units.

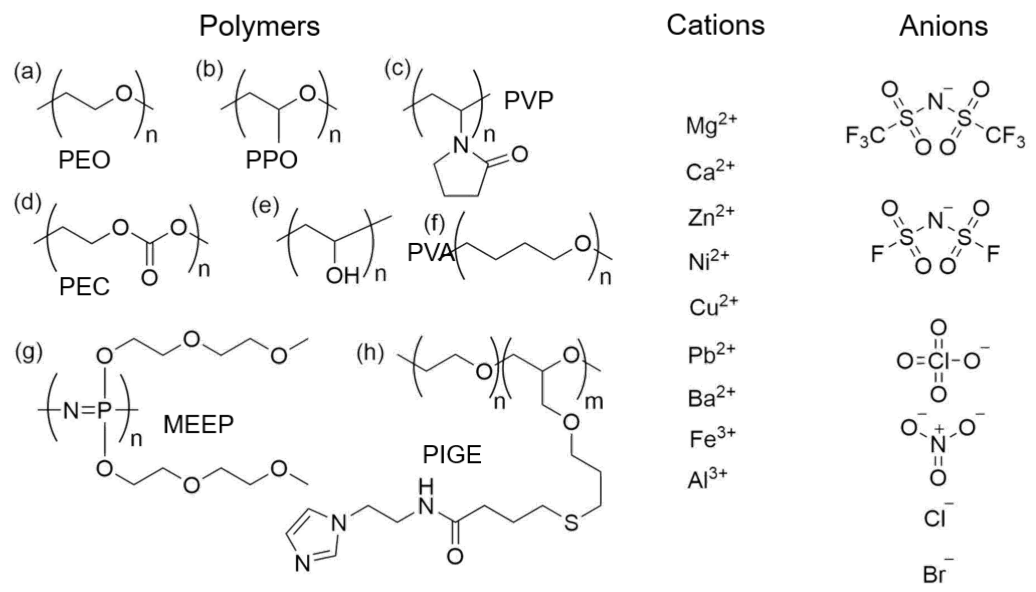

Figure 2. Structures of polymers, cations and anions used for studies of ionic conductivity in multivalent conducting polymers. Most studies have focused on PEO polymers or Mg^{2+} cations.

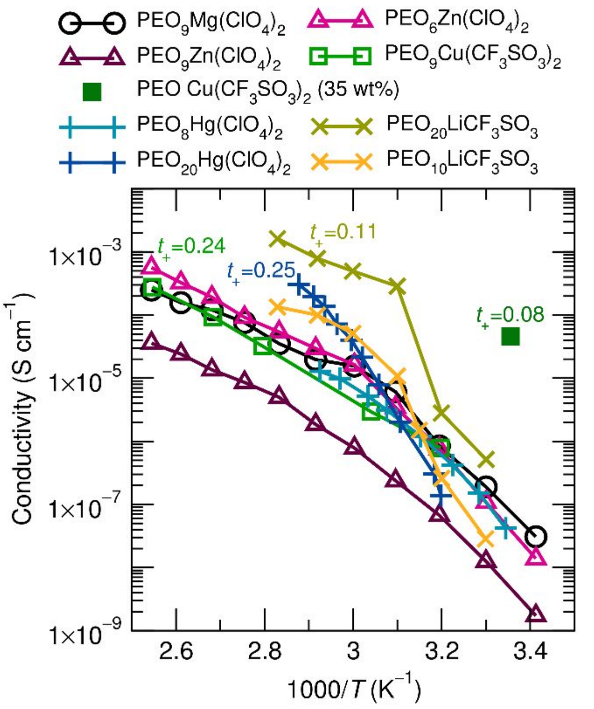

Figure 3. Comparison of ionic conductivity as a function of temperature of a representative set of PEO-based multivalent electrolytes. Cation transference numbers are noted where available. Data references shown in Table 1.

Altering the cation-polymer interaction by incorporating different solvation sites into a polymer can have a profound impact on ionic conductivity behavior, though a lack of systematic and controlled study makes forming conclusions difficult at this time. Magnesium salts mixed into poly(vinyl alcohol) (PVA) show room temperature conductivities ranging from 10^{-7} S cm^{-1} to 8×10^{-4} S cm^{-1} dependent on the anion identity. While magnesium perchlorate conductivity in PEO only reached 10^{-6} S cm^{-1},[58] the same salt mixed with PVA exhibited room temperature conductivity of 10^{-4} S cm^{-1}.[59] Triflate anions likewise exhibited high room temperature conductivity of 5×10^{-4} S cm^{-1},[60] while acetate anions had conductivities around 10^{-7} S cm^{-1}.[61] Addition of $NiBr_2$ into PVA also leads to conductivities of 10^{-5} S cm^{-1} at room temperature.[62] Such high conductivity values are somewhat surprising since the T_g of the PVA systems is around 85 °C. A possible contribution to the ionic conductivity from labile hydroxyl protons and residual water in the system was not considered by any of the above authors. Additional polymer chemistries that have been studied include poly(ethylene carbonate) (PEC) and poly(vinyl pyrrolidone) (PVP), both of which are expected to coordinate with divalent salts via their carbonyl oxygens. In PEC mixed with either a $Mg(TFSI)_2$ or $Mg(ClO_4)_2$ salt, ionic conductivity values remained low at room temperature, at 6×10^{-6} S cm^{-1} for TFSI and 5×10^{-5} S cm^{-1} for ClO_4 at 40 mol% salt addition.[21] PVP mixed with $Mg(ClO_4)_2$ showed much higher conductivities of 5×10^{-4} S cm^{-1} at room temperatures with 40 mol% salt,[63] which is again surprising due to the higher T_g expected for the PVP polymer samples. Importantly, polymer-salt solutions are cast from water or DMSO in all cases and while the electrolytes are dried under vacuum at elevated temperatures, no effort was made to identify the remaining water or solvent content in the materials studied; it is unclear whether the high conductivities reported for some of these electrolytes stem from the effects of solvent impurities. The extent of crystallinity was also not quantified for these alternative polymer chemistries, leading to further variability in performance. Further, no measurements were made of the extent of cation versus anion mobility in these systems, and thus the question remains as to how much the Mg^{2+} or Ni^{2+} cations truly participate in ion conduction.

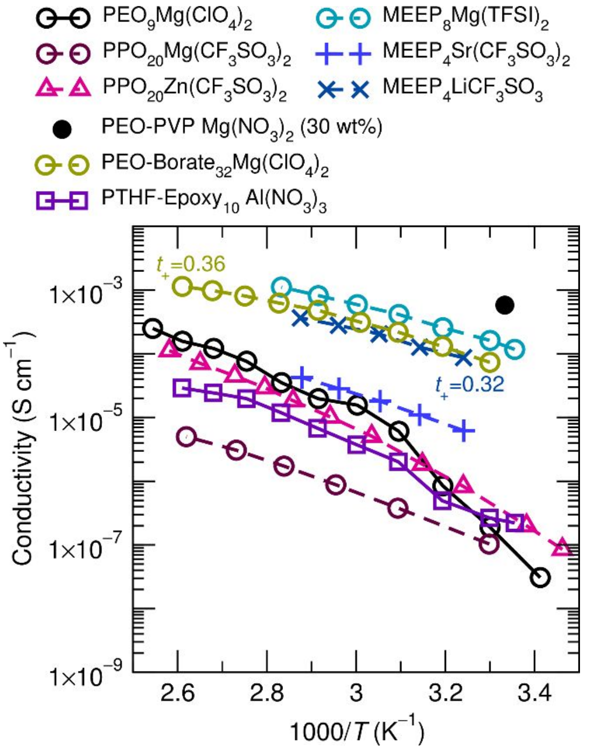

Figure 4. Comparison of ionic conductivity as a function of temperature of a representative set of ether-solvating multivalent electrolytes. Cation transference numbers are noted where available. Data references shown in Table 1.

The addition of a variety of multivalent $TFSI^-$ salts to an imidazole-based polymer revealed that for identical cation concentrations the conductivity remained relatively invariant; slightly higher than Li^+ for Zn^{2+} and Cu^{2+} while slightly lower for Fe^{3+} and Ni^{2+} (Figures 5 and 8).[44] All conductivities were rather low, at around 10^{-5} S cm^{-1} at 70 °C. Since the glass transition temperature remained roughly constant with the various metals at –30 °C, segmental dynamics is not expected to play a significant role in affecting the ionic conductivity. However, teasing out the contribution from the cation species remained challenging, with PFG NMR suggesting an equivalent contribution to the conductivity from the Zn^{2+} as Li^+. The cation contribution from the polymers containing Cu^{2+}, Ni^{2+} and Fe^{3+} could not be studied due to experimental limitations and may exhibit lower cation transference numbers; this could explain the trend of slightly lower total conductivities in the case of Ni^{2+} and Fe^{3+}. These studies suggest there is no significant improvement to the conductivity performance with imidazole-cation interactions as compared with ether oxygen-cation interactions in PEO. In fact diffusion measurements of the anion and Li^+ in the imidazole-tethered polymer and a variant with only ether oxygens and no imidazole (poly(allyl glycidyl ether), or PAGE) showed mobility is faster in the PAGE polymer. It is possible that this is due to solvation site connectivity, which has been shown to play a dominant role in mobility for lithium-polyether systems.[27] Thus, there remains significant opportunity to identify chemistries alternative to PEO that exhibit higher ionic conductivities for multivalent systems.

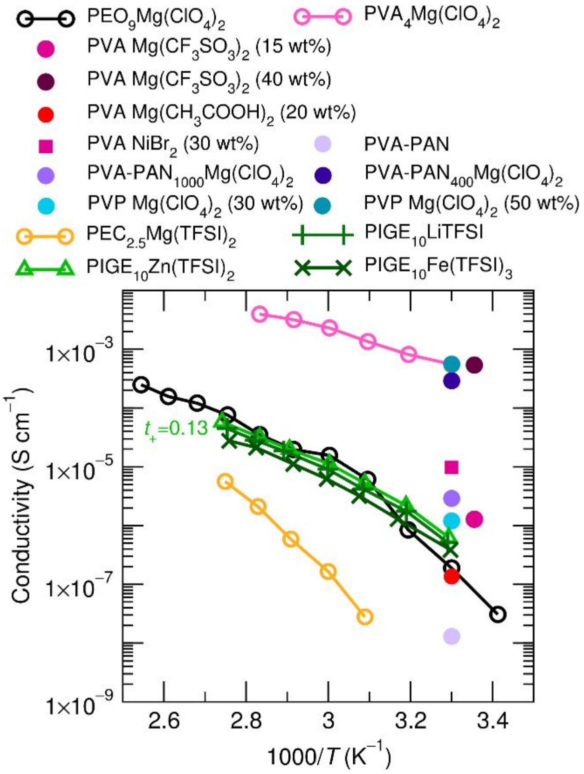

Figure 5. Comparison of ionic conductivity as a function of temperature of multivalent electrolytes with different solvating chemistry than PEO show a wide range of performance, with PVA out-performing other candidates but possibly suspect due to water contamination. Cation transference numbers are noted where available. Data references shown in Table 1.

Ion mobility depends strongly on the glass transition temperature of the polymer electrolyte, and thus it is important to understand how T_g changes with polymer identity and ion identity and concentration. Incorporating polyether moieties into side chains on a more flexible backbone in poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) results in amorphous electrolytes with a lower T_g as compared to PEO and thus higher ionic conductivity (2×10^{-5} S cm^{-1} at 30 °C for MEEP, 10^{-6} S cm^{-1} for PEO) for $LiCF_3SO_3$ (Figure 6).[64] Initial studies showed that ionic conductivity is reduced for divalent and trivalent salts compared to monovalent ones, and transference numbers, measured via steady-state polarization without accounting for changes in interfacial resistance, were reasonable for Li^+ but immeasurable for Zn^{2+}.[64] More recent work suggests that the ionic conductivity in MEEP is similar between Li and Mg versions of the same salts (triflate and TFSI), though the salt concentration for maximum conductivity differs between Li^+ and Mg^{2+}.[65] This study suggests an amorphous polymer with a highly mobile backbone can improve conductivity at least for Li^+, regardless of possibly worse solvation site connectivity in side-chain ethers compared to PEO.

PEO and similar polymer electrolytes exhibit a maximum in ionic conductivity as a function of salt concentration.[20] Cation-polymer interactions create weak dynamic crosslinks which slow segmental motion as salt concentration is increased. Thus, ion mobility is reduced at high salt concentration due to an increase in T_g.[66] Such behavior is seen in a number of multivalent polymer systems, including both those with ether oxygens as the primary solvating units and those with different ion-polymer interactions such as Ni^{2+}-imidazole.[33, 67] The strong complexation of cationic species by the polymer solvating units in such systems results in the formation of longer-lived temporary crosslinks which slow down segmental dynamics. In these systems, increasing salt concentration is inherently at odds with segmental dynamics, and an optimal salt concentration exists for maximum conductivity.

While there have also been observations of decreasing T_g with increasing salt concentration, such as for PVA and PEC-based electrolytes, the ionic conductivity still generally shows a maximum at intermediate salt content. For PVA systems, the T_g decreases from 85 °C upon the addition of both Mg^{2+} or Ni^{2+} salts.[61-62] Some researchers suggest this is due to the plasticizing effect of the typically bulky and polarizable anions, though the decrease in T_g was also observed for $NiBr_2$ salts.[62] Another explanation is the disruption of hydrogen bonding in PVA upon salt addition leading to increased segmental dynamics. It would further be interesting to identify what role any residual solvent plays in the T_g decrease, as most electrolytes were cast from water or other high boiling point solvents. A decrease in T_g with salt addition was also observed for PEC-based electrolytes, both with LiFSI addition[22] as well as $MgTFSI_2$ or $Mg(ClO_4)_2$.[21] For the Li-system, NMR and DFT suggest a loose coordination structure between the Li^+ cation and the carbonyl solvating group. These weak interactions could allow for plasticizing effects from the bulky anions to dominate the T_g trend rather than the dynamic cross-linking that occurs between neighboring polymer chains solvating the same cation. It is possible that similar plasticizing effects dominate for the Mg^{2+} salts. For all but one of the above systems,[60] the ionic conductivity as a function of concentration still exhibits a maximum at intermediate concentrations. This suggests that while T_g may be important to an extent in determining ionic conductivity, other factors dictating ion mobility such as ion-ion interactions also govern ionic conductivity.

Ion-ion interactions in polymer electrolytes typically reduce ion mobility and ultimately result in decreasing ionic conductivity as a function of salt concentration. Such ion aggregation is typically ill defined in polymers but is critical in dictating performance. The strong electrostatic interactions between anions and multivalent cations can result in more significant ionic clustering in multivalent polymer systems and contributes to lower conductivity. The existence of ion pairings has been demonstrated through FTIR and Raman studies of the vibrational modes of commonly used anions such as triflate (CF_3SO_3) for multivalent cations in PEO and PPO.[56, 58, 68-71] Due to its stronger ability to coordinate cations, PEO showed higher concentrations of free anions than PPO.[56] In general, di- and tri-valent species show increased aggregation because they more strongly bind to their respective anions compared with Li^+, though interestingly this is not the case for Cu^{2+} in PEO.[69] The authors do not provide rationalization for this observation. While the IR study suggests Cu^{2+} exhibits less ion pairing in PEO compared with Li^+, the ionic conductivity of $LiCF_3SO_3$ salt in PEO was still reported to be higher than that of $Cu(CF_3SO_3)_2$,[33] conceding that ion pairing is only one of many factors affecting ionic conductivity. Ion pairing was also suggested to be the reason for a maximum in ionic conductivity as a function of concentration of $Mg(ClO_4)_2$ in PEO.[58] At higher ion concentrations, the population of "free" anions was reduced, signifying a larger proportion of ion pairing. However, this study did not discuss other factors such as the effect of T_g which could be playing a concurrent role in the decrease in conductivity with concentration. Interestingly, for magnesium salts added into PEC, FTIR analysis suggests mostly free anion species, possibly due to the higher polarizability of the PEC polymer as compared to PEO.[21] Since most of the polymer electrolytes studied for both mono- and multivalent conduction have low polarizability and thus low dielectric constant, this is a synthetic area that can be pursued further. The challenge is to identify moieties which can be added to a polymer system for improved charge screening without reducing the mobility of cation species.

Anion-cation interactions arising from incomplete salt dissociation can also result in larger scale concentration fluctuations or aggregation which can be predicted computationally[72] and detected experimentally using X-ray scattering and TEM[73] or AFM.[60] Significant work has been done in this area for monovalent ion-containing polymers and on single-ion conductors where one ion is tethered to the backbone; both the valency and ion tethering could affect the propensity for aggregation to occur. Significant ion aggregation is identified for poly(styrene sulfonate)-based systems neutralized with a variety of monovalent (Na^+, Cs^+) or divalent (Mg^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}) cations.[73] Interestingly, the ion aggregate size seems to scale only with cation size rather than valency, though this does not account for changes in ion concentration due to a divalent cation neutralizing two sulfonate groups instead of just one. Aggregation can also be probed via AFM and has been used to identify the inhomogeneity in PVA containing varying concentrations of $Mg(CF_3SO_3)_2$.[60] This technique only works well if there is a significant change in material hardness (e.g. T_g) upon salt addition to differentiate high versus low salt concentration regions. It was suggested that aggregation occurs at all concentrations of $Mg(CF_3SO_3)_2$, and ionic conductivity improves as the connectivity of this aggregation increases. The challenge of determining the connectivity of ionic aggregation is well-known within the ionomer community and relevant for the performance of multivalent ion conducting polymers. Concentration fluctuations causing inhomogeneities on the order of a few nanometers to hundreds of nanometers are likely to affect the mobility of ions moving through the bulk of a polymer electrolyte. Thus, the morphology and connectivity of such aggregates is important. Morphologies can range from spherical to stringy to percolated,[72] with percolation likely improving ion conduction through the polymer network. Much of this work is limited to ionomers and may be relevant for single-ion conducting electrolytes, but might present different results compared with salt-in-polymer systems where both the anions and cations are mobile relative to the polymer matrix. Thus, further opportunities exist for computational and experimental understanding of the extent of ion aggregation in multivalent polymers and the role of aggregate morphology on bulk conductivity.

III. Mechanical property control in multivalent ion conductors

Multivalent ions within ion-conducting polymers may provide beneficial mechanical properties compared to their lithium counterparts. The use of polymer electrolytes in devices enables safer, simpler and more flexible device design if the polymer can act as both the separator and the electrolyte. This requires a robust polymer membrane. Most studies of multivalent polymer electrolytes have focused on ionic conductivity, but not on the mechanical properties of the resulting films.

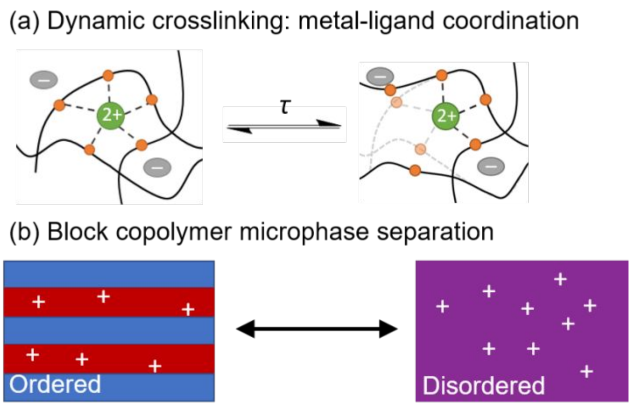

Figure 6. Mechanical properties of multivalent polymers can be tuned through (a) the use of metal-ligand coordination as well as (b) their incorporation into block copolymers. For both strategies, the identity of the metal can dictate the extent of mechanical property improvement as well as the impact to ionic conductivity.

Multivalent ions are known to impart tailorable mechanical properties for polymer networks and gels. Specifically, multivalent ions such as Ni^{2+}, Cu^{2+}, Zn^{2+} and Fe^{3+} can be used as dynamic crosslinking agents for self-healing or stimuli-responsive polymer networks due to their multi-functional interactions with the polymeric host, [74-79] though the balance between transient cross-linking and ionic conductivity has not been exploited (Figure 6a).

Recent work from our group has shown that ion-conducting polymer networks form through the interaction of Ni^{2+} salts with imidazole ligand coordination sites on a polymer chain.[67] At all studied salt concentrations, a dynamically crosslinked network was formed, showing the typical rheological signature of a plateau in the storage modulus, followed by subsequent liquid-like relaxation at lower frequencies. The plateau modulus increases as a function of salt concentration but saturates at around eight times the original value of 1 MPa upon complete crosslinking of the gel. During the initial increase in plateau modulus, there is a concomitant improvement in ionic conductivity due to the higher ion concentration. At Ni^{2+} to imidazole ratios larger than 0.12, however, the ionic conductivity decreases due to dominant effects of an increasing T_g. The influence of the slower segmental dynamics is apparent when the temperature at which conductivity is measured is adjusted by the T_g at each salt concentration; the ionic conductivity then shows a monotonic increase with salt concentration. Thus, multivalent metal cations can act as dynamic cross-linking agents only at low concentrations, before slower segmental motion dominates the behaviour and reduces ionic conductivity. Importantly, this initial study did not probe the extent to which the Ni^{2+} cation participates in ion conduction. While the labile nature of the metal-ligand coordination bond allows for cation conduction in such a system, the strong interaction between the Ni^{2+} and imidazole likely reduces cation mobility such that the anion conduction dominates as in most polymer electrolytes.

A follow-up study examined how a wider range of multivalent salts could be used to control polymer mechanical properties.[44] Li^{+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Fe^{3+} salts were mixed at a constant ratio of cation to imidazole of 0.1 into the same polymer matrix as before. The specific coordination chemistry of the metal cation with imidazole results in dramatic tunability of the zero-frequency viscosity of the polymer systems, with over three-orders of magnitude change between the Li-PIGE polymer and the Ni-PIGE polymer (Figure 7). Interestingly, the ionic conductivity does not follow a specific trend and is much less sensitive to salt identity than the bulk mechanical properties. One likely contribution to this insensitivity is the invariant T_g as a function of metal cation identity; thus, while bulk viscosity can be altered by switching metal-ligand coordination strength, the local segmental dynamics remain essentially invariant, suggesting that ion mobility through the polymer matrix is likely not significantly affected. Such behavior has also been observed for covalent crosslinking in ion-conducting polymers with low crosslinking density and flexible crosslinkers.[80] Indeed, the PFG NMR diffusion coefficient of the $TFSI^{-}$ anion in the Li^{+}- and Zn^{2+}-containing polymers is identical once adjusting for the slight T_g change in the two polymers. This suggests that ion-ion interactions are minimal, as the identity of the cation and concentration of the anion do not play a role in the mobility of the anion species. In this study, PFG NMR suggests that the Zn^{2+} ions are mobile and contribute similarly to the ionic conductivity in the Zn-PIGE as the Li^{+} ions do in Li-PIGE. These results motivate future studies to explore the ability of divalent species to both contribute to the ionic conductivity as well as impart beneficial mechanical properties to polymer electrolytes.

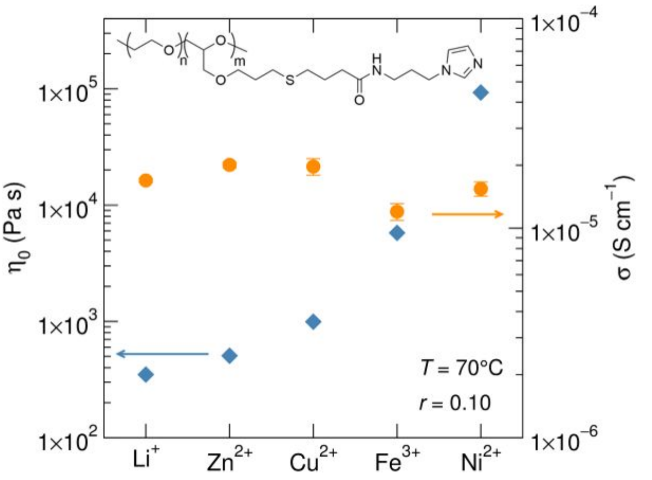

Figure 7. Metal-ligand coordination using multivalent cations can impart significant changes to bulk mechanical properties such as the zero-frequency viscosity while insignificantly impacting total ionic conductivity. Figure adapted from Schauser et al.[44]

An orthogonal strategy towards decoupling the ionic conductivity from the mechanical properties of polymer electrolytes is the use of nanostructured block copolymers (BCPs) (Figure 6b). In such system designs, the ionic conductivity is imparted by a polymer such as PEO mixed with salt, which is covalently bound to a second, mechanically rigid and glassy block such as polystyrene (PS). Microphase separation, typically into a lamellar morphology, enables the two polymers to play their separate roles in determining the properties of these electrolytes. While a decrease in ionic conductivity is seen compared to homopolymer PEO due to the addition of an insulating phase, a dramatic improvement in mechanical rigidity of these electrolytes makes up for the slight decrease in conductivity performance.[81] Further small improvements to the mechanical properties as well as the conductivity can be achieved through bi-continuous morphologies such as gyroid, which can be accessed through end-group modification for low molecular weight systems.[82-83] Similar studies on multivalent salts in BCPs have not been performed but would provide interesting comparisons in their effect on ionic conductivity and mechanical property retention as compared with lithium counterparts.

Work on multivalent Mg^{2+} block copolymer electrolytes has focused on single-ion conductors and has been less successful in decoupling conductivity and mechanics as compared to the conventional salt-containing BCPs. In these systems, the anion is tethered to the PS block in the copolymer; upon incorporation of the PEO block, the cation tends to dissociate from the anion and reside in the PEO-solvating domains.[84] Unfortunately, for Li^+ single-ion conducting BCPs, cation dissociation and subsequent solvation by the PEO block results in favorable interactions between the two blocks and a lack of microphase separation, eliminating mechanical property improvements until a third incompatible block is added, such as PS without tethered anions.[84] Unlike the Li^+ polymer, the Mg^{2+}-containing polymer shows weak phase separation, which imparts multiple orders of magnitude improvement to the shear modulus of the resulting films.[85] However, this phase separation likely stems from the incomplete dissociation of the Mg^{2+} cation from the tethered anion, and thus overall ionic conductivity is substantially reduced due to the lower concentration of mobile cations.[85]

Additional efforts to improve conductivity and mechanical performance in this area could stem from two approaches. First, since it seems that salt dissociation for single-ion diblock copolymers tends to lead to disordered systems, the incorporation of a third mechanically robust block is necessary to fully recover the original high shear modulus behavior. Further, since the block with the tethered anion does not provide significant mechanical advantage and indeed generally mixes with the ion-conducting block, tethering of the anion to a lower T_g backbone, or direct incorporation into the ionically conducting block could enable improvements in the measured ionic conductivity.

IV. Future outlook

A key question for multivalent polyelectrolyte design is how to achieve high ion concentration while concurrently increasing multivalent ion mobility (Figure 8). This requires controlling salt dissociation separately from ion mobility within the polymer matrix. Traditional polymer electrolyte design does not decouple these two factors, as the species within the polymer that improve salt dissociation also bind tightly to the cation. Ion concentration is controlled by both the choice of counterion as well as by the polymer dielectric environment. Ion mobility depends on the identity of the multivalent cation and the design of the coordinating ligand. Increasing ion mobility requires improving the frequency of ion exchange between coordination sites in a polymer matrix, which is especially challenging for multifunctional ions which interact with multiple sites within a polymer at once.

The complexity of the synthetic considerations as discussed in section II illustrates the challenge in the directed design of multivalent conducting polymer electrolytes. Most work has focused on PEO polymers, though a small number of studies on alternative chemistries are intriguing and merit further detailed examination. Opportunities exist for computational studies to screen for promising candidates for multivalent conduction by identifying systems for which ion-polymer interactions are labile, aggregation is low, and solvation structure enables percolated networks for ion transport. The lability of metal-polymer interactions can be tuned by using different coordinating groups whose geometry or strength of interaction may increase the kinetics of ligand exchange. While ligand exchange kinetics have been measured for a variety of divalent species and small-molecule ligands in aqueous solution, such trends may not translate to dry polymer systems[35] since exchange in aqueous solution is typically dominated by water molecules.[44] Hard-soft acid-base theory can be used as a predictor for the binding strength of multivalent cations to various potential ligands, although factors including the ligand-field stabilization energy are important for transition metal complexes. An understanding of ion transport mechanism can also be gained from a look at the activation energy (E_a) for ionic conductivity as a function of temperature; most polymers follow a VFT temperature-dependence above their T_g and Arrhenius behavior below T_g. Higher E_a suggests more hindered ion motion. Still, few polymer studies calculate E_a (Table 1); improved reporting and analysis of the E_a of ion transport for multivalent systems could shed light on favorable polymer chemistries for cation transport.

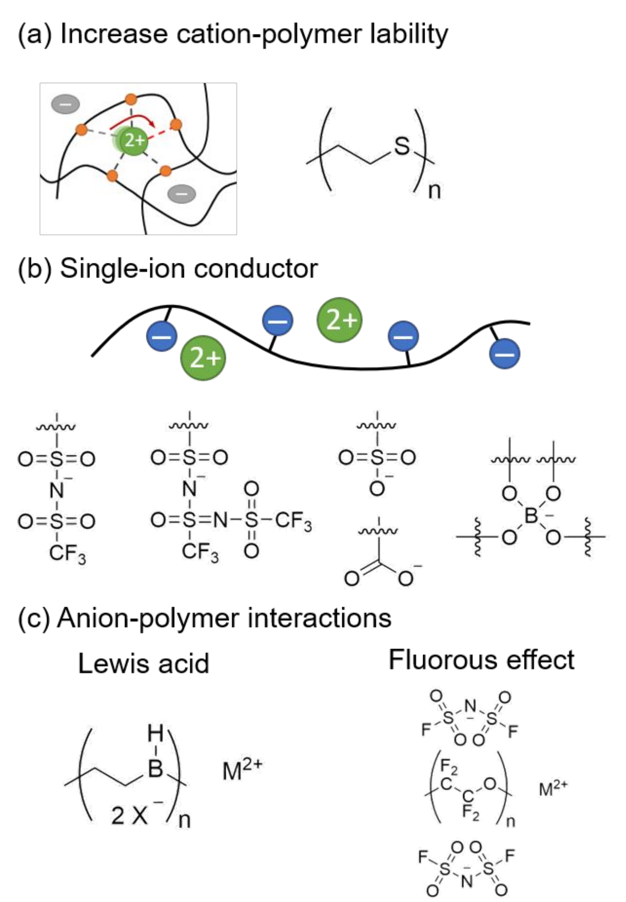

Figure 8. Alternative opportunities exist for improving fundamental understanding as well as performance of multivalent cation conduction in polymer electrolytes. These include the design of (a) single-ion conductors such as those already developed for lithium-ion conduction, (b) polymers which preferentially interact with anion species, and (c) solvating moieties that have more labile interactions with multivalent ions.

A first-principles study on the lability of Li^+ in PEO, PEI $(CH_2CH_2NH)_n$ and PES $(CH_2CH_2S)_n$ suggests that PES forms more labile bonds with Li^+ compared to both PEO and PEI and thus can provide higher Li^+ mobility.[86] To follow up on this work, a series of poly(ether-thioethers) with varying carbon linkers and thioether to ether ratios were investigated with LiTFSI salt.[87] FTIR confirmed both the ether and thioether moieties solvate the added salt, and all exhibited similar conductivities. It was suggested that a shorter carbon spacer improves conductivity, but identification of the importance of ether versus thioether groups for conductivity remained elusive. A recent comprehensive review summarizes the work for lithium solid polymer electrolytes using chemistry distinct from polyethers, suggesting that even here there is much room for improvement in ionic conductivity compared to PEO due to a decoupling of ion conduction from T_g.[23]

Initial work for multivalent systems with varying chemistry has suggested similar high conductivity even in high T_g materials. Further synthetic work on such alternative chemistries and repetition with multivalent ions is warranted, though trends that work well for alkali metals might not hold for transition metal cations. Computational prediction of exchange, through the identification of transition-state activation energies, in new polymer chemistries and for multivalent ions would provide a powerful platform for the design of more labile interactions.

It is also possible to design polymers in which the solvating groups primarily interact with the anion rather than cation species through the addition of either Lewis-acidic moieties into the polymer[88-89] or other groups that preferentially solvate specific anions, such as fluorination of the polymer backbone to sequester fluorinated anions.[90] A PEO-based network with boroxine ring crosslinkers acts as an anion trap and increases Li^+ transference numbers to 0.75 for bulky salts such as $LiCF_3SO_3$ and $LiBF_4$, with additional improvement to 0.88 for LiCl.[91] Similar studies were performed for borate ester networks mixed with Mg^{2+} salts with perchlorate, triflate and $TFSI^-$ anions.[92-93] Ionic conductivities on the order of 10^{-5} S cm^{-1} were measured at room temperature, and transference numbers ranged from 0.20 to 0.51 with smaller anions showing better transference numbers but lower conductivity at equivalent temperatures.[93] Increasing the concentration of anion traps also increases the transference number.[92] The transference number measurements were performed using DC polarization without adjustment for interfacial resistance changes over time and could thus be inaccurate, though the general trends between the studied anions and boron concentrations should still hold. Further work in this area could provide promising performance improvements for multivalent polymer electrolytes.

Identifying the connectivity of solvation sites through the polymer can also play a large role in screening for polymer candidates. One such study performed for Li-polyether conductors was influential in determining that the reason for the high conductivity of PEO over other polyethers and esters was due to the high percolation of solvation sites in PEO which result in more facile Li^+ transport.[57] This ambitious study highlights the complexity of designing a polymer electrolyte from the ground up; specifically, the effects of segmental dynamics, solvation strength, and solvation connectivity interact synergistically to determine ultimate conductivity. Thus, electrolyte design cannot solely focus on the incorporation of labile coordinating moieties, high dielectric constant and high segmental dynamics, but must also consider polymer architecture and its effect on the proximity of neighboring solvation sites for ion transport. Characterizing similar solvation trends for alternative polymer chemistries and architectures would enable screening for possible candidates before investing significant synthetic effort.

To determine the efficacy of synthetic strategies in improving cation mobility, it must be possible to accurately measure the contribution of multivalent cations to the measured total conductivity. Transference number measurements using traditional techniques are extremely variable, likely because the underlying assumptions of ideal electrolytes with dissociated ions are not valid for many of the multivalent electrolytes. What is needed is a technique that enables measurement of ion mobility without convolution from interfacial processes or aggregate species. Perhaps most promising is the use of concentration and diffusion cells to measure thermodynamic parameters, as was done recently in the case of Li^+-PEO, though there may still be issues with large interfacial resistances.[28]

There is also the option to circumvent such transport questions completely through the design of single-ion conductors (Figure 8). Significant effort in the field of single-ion conductors has focused on lithium,[94] while almost no work on multivalent polymers for ion conduction has been performed other than the block copolymer work mentioned above.[84-85] For monovalent systems, it is known that improving cation mobility through dissociation from the anion is critical for enhancing conductivity,[95] as is reducing the glass transition temperature of the polymer. It is currently common practice to tether a $TFSI^-$ anion to a polystyrene-based backbone, though work on lower T_g backbones has been reported,[96-97] as has the use of different tethered anions such as sulfonates[98] or borates.[99-100] The more delocalized the anion, the higher the conductivity due to improved cation mobility;[95] thus sulfonates or carboxylates are not a great choice and result in lower conductivities,[101-102] while the use of delocalized tethered anions has enabled ionic conductivities on the order of 10^{-4} S cm^{-1} at 90 °C.[95] The addition of a small molecule complex containing boron ($BF_3{\cdot}OEt_2$) enabled improved dissociation of Li^+ from a carbonate anion-tethered polymer due to preferential boron-anion interactions.[102] A recent review summarizes advances and future opportunities for lithium-based single-ion conductors.[94] Similar concepts can be applied for multivalent systems, with the additional caveat that dynamic ionic crosslinking between cations and anions from multiple chains may play an important role in polymer segmental dynamics. The incorporation of solvating groups within the polymer that can preferentially interact with the cation species to enhance dissociation but enable mobility will be critical, as will the proximity between anion and solvating groups.[101]

Multivalent polymer electrolytes also present opportunities for mechanical property enhancement compared to their monovalent counterparts. One set of studies identified significant enhancement of bulk mechanical properties through the inclusion of multivalent metal-ligand coordination interactions within a polymer matrix, with minimal effects on the total ionic conductivity.[44] However, further work in such systems must be performed to identify the extent of cation mobility in a system where it also acts as a dynamic cross-linker. The ability for some cations, such as Ni^{2+} or Fe^{3+}, to dramatically enhance mechanical properties could also be used orthogonally, with the addition of those cations for the sole purpose of enhancing polymer mechanics while the ions of interest (e.g. Mg^{2+}, Zn^{2+}) are added separately for ionic conductivity. Further opportunities exist in the realm of block copolymers, both in terms of conventional block copolymers with salt addition and single-ion work. The synthetic strategies mentioned above can be employed for the ion-containing block, while an inert block is added for mechanical stability.

A feature that has been largely overlooked in this perspective and in many fundamental studies is the design of multivalent ion conductors that are compatible with the broader device architecture in energy applications. That is, the polymer electrolyte must be electrochemically stable against the anode and cathode material, as well as towards the current collectors and casing materials. Previous studies, especially for Mg-based polymer electrolytes, have shown increasing interfacial resistances over time, as well as extremely large overpotentials required for Mg^{2+} deposition and stripping.[37] This poses challenges for the implementation of such systems in applications. Thus, it is important to consider stability and compatibility concurrently with polymer electrolyte design.

Conclusion

Strategic design of multivalent ion conducting polymers remains an elusive but feasible goal requiring more systematic studies, computational predictions, and expanded synthetic approaches. Polymer electrolyte performance hinges on increasing both the concentration and mobility of cation species. The multifunctional interactions of multivalent ions with a polymer matrix typically reduces both salt dissociation and ion mobility compared to Li^+. New polymer chemistries may enable more labile cation-polymer interactions and higher conductivity. Ion transport in polymers is typically dominated by anion contributions; thus, understanding how ion and polymer identity affect cation transport in multivalent systems will be critical for improved performance. This can be achieved through better transference number measurements or through the design of novel single-ion conducting polymer electrolytes to eliminate anion mobility. Future systematic studies are required to develop targeted design rules for multivalent ion conduction. Synthetic and computational work should focus on developing polymer chemistries with high dielectric constants, labile ion-polymer interactions, and solvation site connectivity to enable the development of safer and higher performance multivalent electrolytes.

Table of polymer chemistries and multivalent salts plotted in Figures 3-5.

Polymer	Salt	Concentration[a]	Casting solvent	Conductivity in S cm^{-1} [b]	Activation Energy (eV)	Transference number	Reference
PEO	$Mg(ClO_4)_2$	1/9	Methanol	1.9×10^{-7} (30°C)	N/A	N/A	[54]
PEO	$Zn(ClO_4)_2$	1/9	Methanol	1.25×10^{-8} (30°C)	N/A	N/A	[54]
PEO	$Zn(ClO_4)_2$	1/6	Methanol	1.1×10^{-7} (30°C)	N/A	N/A	[54]
PEO	$Cu(FSI)_2$	1/9	Acetonitrile	7.9×10^{-7} (40°C)	N/A	0.24[e]	[103]
PEO	$Cu(FSI)_2$	35.4 wt%	Acetonitrile	4.6×10^{-5} (25°C)	N/A	0.08[e]	[32]
PEO	$Hg(ClO_4)_2$	1/8	Acetonitrile	1.5×10^{-7} (32°C)	N/A	N/A	[34]
PEO	$Hg(ClO_4)_2$	1/20	Acetonitrile	1.4×10^{-7} (40°C)	N/A	0.25[e]	[34]
PEO	LiFSI	1/20	Acetonitrile	5.2×10^{-7} (30°C)	N/A	0.11[e]	[104]
PEO	LiFSI	1/10	Acetonitrile	2.9×10^{-7} (30°C)	N/A	N/A	[104]
PPO	$Mg(FSI)_2$	1/20	Acetonitrile	1.0×10^{-7} (30°C)	N/A	N/A	[56]
PPO	$Zn(FSI)_2$	1/20	Acetonitrile	8.3×10^{-7} (35°C)	N/A	N/A	[56]
PTHF-Epoxy	Al(NO3)3	1/10	Tetrahydrofuran	2.6×10^{-7} (30°C)	N/A	N/A	[105]
MEEP	LiFSI	1/4	N/A	8.7×10^{-5} (35°C)	N/A	0.32[e]	[64]
MEEP	$Sr(FSI)_2$	1/4	N/A	6.2×10^{-6} (35°C)	N/A	N/A	[64]
MEEP	$Mg(TFSI)_2$	1/8	Tetrahydrofuran	1.6×10^{-4} (30°C)	0.07 [c]	N/A	[65]
PEO-PVP blend	$Mg(NO_3)_2$	30 wt%	Methanol	5.8×10^{-4} (27°C)	0.31 [d]	N/A	[37]
PEO-Borate	$Mg(ClO_4)_2$	1/32	N/A	7.3×10^{-5} (30°C)	N/A	0.36[e]	[106]
PVA	$Mg(ClO_4)_2$	1/4	Water	5.5×10^{-4} (30°C)	0.38 [d]	N/A	[59]
PVA	$Mg(FSI)_2$	15 wt%	DMSO	1.3×10^{-6} (25°C)	N/A	N/A	[60]
PVA	$Mg(FSI)_2$	40 wt%	DMSO	5.4×10^{-4} (25°C)	N/A	N/A	[60]
PVA	$Mg(CH_3COOH)_2$	20 wt%	Water	1.4×10^{-7} (30°C)	N/A	N/A	[61]
PVA	$NiBr_2$	30 wt%	Water	9.8×10^{-6} (30°C)	0.3 [d]	N/A	[62]
PVA-PAN	N/A	N/A	DMF	1.3×10^{-8} (30°C)	1.33 [d]	N/A	[36]
PVA-PAN	$Mg(ClO_4)_2$	1/1000	DMF	2.9×10^{-6} (30°C)	0.66 [d]	N/A	[36]
PVA-PAN	$Mg(ClO_4)_2$	1/400	DMF	2.9×10^{-4} (30°C)	0.21 [d]	N/A	[36]
PVP	$Mg(ClO_4)_2$	30 wt%	Water	1.2×10^{-6} (30°C)	N/A	N/A	[63]
PVP	$Mg(ClO_4)_2$	50 wt%	Water	5.6×10^{-4} (30°C)	N/A	N/A	[63]
PEC	$Mg(TFSI)_2$	1/2.5	Acetonitrile	2.8×10^{-8} (50°C)	0.2 [c]	N/A	[21]
PIGE	LiTFSI	1/10	Methanol	5.1×10^{-7} (30°C)	N/A	0.18[f]	[44]
PIGE	$Zn(TFSI)_2$	1/10	Methanol	6.3×10^{-7} (30°C)	N/A	0.13[f]	[44]
PIGE	$Fe(TFSI)_3$	1/10	Methanol	3.9×10^{-7} (30°C)	N/A	N/A	[44]

[a] Concentration given as either weight percent or ratio of salt to number of monomer units in polymer. [b] Conductivity measured using ac impedance, with the temperature noted in parentheses. [c] Activation energy calculated from VFT fit. [d] Activation energy calculated from Arrhenius fit. [e] Transference number measured via chronoamperometry. [f] Transference number measured via NMR.

Journal Name

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Conflicts of interest

There are no conflicts to declare.

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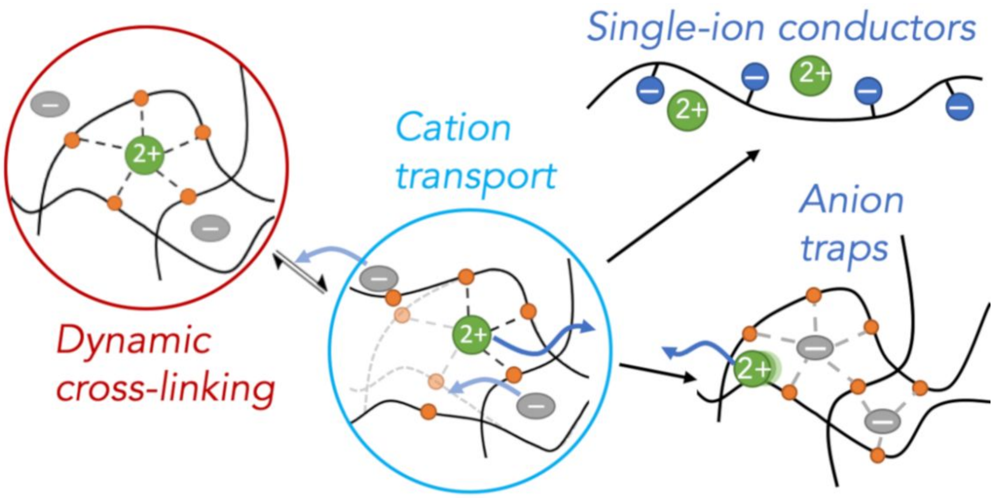

The multifunctional interactions of multivalent cations with polymers creates challenges for enhancing cation conductivity, which may be solved through new synthetic and computational efforts.