# Superionic behavior in polyethylene-oxide–based single-ion conductors

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(Received 12 May 2013; revised manuscript received 13 August 2013; published 13 November 2013)

We demonstrate superionic ion conduction in simulations of a poly(ethylene oxide)-based polymer electrolyte. The superionic conduction uses cation hopping via chain-like ion aggregates, enabling long-range charge transfer while ions only move locally. The Na single-ion conductor achieves two essential features of superionic metal ion conductors: one-dimensional ion structure and immobile anions. The superionic conduction depends on the number and length of conduction pathways, the conduction pathway lifetime, and the rate at which end ions join and leave the pathway.

DOI: 10.1103/PhysRevE.88.052602 PACS number(s): 36.20.Ey, 36.90.+f, 66.30.hk, 74.70.Kn

## I. INTRODUCTION

Solid electrolytes are important technologically, in particular for Li batteries, because they reduce dendrite formation and improve safety. In addition to crystalline conductors, there are two types of ion conducting amorphous conductors: elastomeric polymer-salts and inorganic glasses [1–3]. It is generally recognized that the mechanism for conductance in polymer-salts is intrinsically different from that in vitreous glasses [4]. Polymer-salts have flexible polymer backbones, and conduction is coupled with polymer motion. Good performance for elastomers thus depends on the operating temperature being far above the glass transition temperature $T_g$, resulting in conductivity of $10^{-4}$–$10^{-6}$ S/cm at room temperature and practical conductivity (i.e., $10^{-2}$–$10^{-3}$ S/cm) at elevated temperatures. For vitreous conductors, the requirements of dimensional stability and stability against devitrification demand the operating temperature be far lower than $T_g$. Hence the conduction mechanism must be independent of matrix motion and instead is dependent on arrangement of coordination sites. One ion (usually an anion) serves as a local coordination site, allowing the other ion (usually a cation) to hop, thus promoting ion diffusion. The conduction mechanisms in both types of amorphous conductors are a popular research question because it is difficult to directly observe ion motion.

Superionic behavior, defined as charge diffusion in excess of ion diffusion, has been observed in vitreous systems, such as AgI [5–8], $Ag_2Se$ [9,10], CuI [11], CuBr [12], $CaF_2$ [13,14], $PbF_2$ [14,15], and alkali-oxide–$SiO_2$ glasses [16,17]. Superionic conduction has not been reported for elastomeric polymer salts but would be very advantageous because the decoupling of ion and polymer motions permits high conductivity coupled with a stiff material. Such a material would be ideal in Li batteries because stiffness is required to prevent dendrite growth in the presence of a Li metal anode. Characteristic features of superionic vitreous conductors are the large mobility difference between cations and anions [18–21], similar cation-cation and cation-anion association distances [22–25], large spatial fluctuations of the mobile ion distribution [23,24], and one-dimensional streams leading to collective motion [18,19,22–27]. The large difference between cation and anion mobility allows cations to migrate between sites in the sublattice of immobile anions. While immobile anions distribute evenly, the cations are found to be partially covalent bonded (due to reduced charge transfer between unlike ions), resulting in large fluctuation in their density distribution [28,29]. This results in similar cation-anion and cation-cation distances together with the reduced cation Coulomb repulsion, allowing cations to quickly move between sites. Such ion distributions are not observed in similar but nonsuperionic materials, suggesting that these also enable charge diffusion over large distances. Several models of one-dimensional collective motion, such as the caterpillar mechanism [8,30–33], have been suggested, but no theory of charge conduction in superionic materials has yet received general acceptance [34]. Recently, a study on superionic $LiMgSO_4F$ observed collective motion that conducts charge via one-dimensional “Li-ion channels,” [35] where one Li ion joins a Li channel from one end, ejecting another Li ion at the opposite end.

In this paper, we report superionic conduction for a poly(ethylene oxide)-based Na single-ion conductor (PEO600Na in Fig. 1), in which a benzene sulfonate anion is incorporated in a polyethylene oxide (PEO) backbone using an isophalate group [36]. Using a 700 ns run, we push to times long enough to assess charge diffusion and clearly see the hallmark of superionic conduction. We compare PEO600Na to four similar but not superionic systems [37–39] and determine that superionic conductivity requires intermediate size chain-like aggregates with stable conduction pathways that remain in place long enough for superionic conduction events.

## II. METHODS

A model of PEO600Na is available and provides a good description of both structural and dynamic behavior [38]. To investigate how chain-like aggregates affect charge transport, we present data for this model at 343 and 423 K, where the anion delocalization is altered to strengthen and weaken cation-anion interaction [39] and the PEO-salt analog (anions free to move) of this model [38]. All five models are simulated at the atomistic level, using united atoms for methylene groups. The models have the same number of PEO monomers (52 monomers), polymers (27 chains), and ions (108 cations and 108 anions), resulting in cubic simulation cells with a length around 50 Å. Moreover, these models have different degrees

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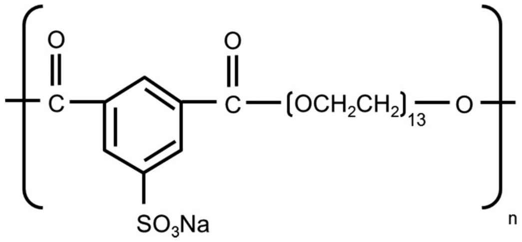

FIG. 1. Chemical structure of the PEO-based single-ion conductor, PEO600-Na.

of ion aggregation and ion mobility, allowing us to investigate the relationship between charge transport and ion chain-like aggregates. We use LAMMPS [40] to carry out the molecular dynamics simulations until charge diffusion is achieved. The simulations are under a *NVT* ensemble, with 343 K and 1 atm.

To assess superionic behavior, we compare the tracer diffusion coefficient $D$ and the diffusion coefficient derived from the ionic conductivity $\sigma_e$:

$$D_e = \frac{V k_B T \sigma_e}{e^2 N}, \tag{1}$$

where $V$ is the volume, $k_B$ is Boltzmann's constant, $T$ is the temperature, $e$ is the electron charge, and $N$ is the number of ions. Because it is based on the conductivity, $D_e$ is also referred to as charge diffusion, as opposed to tracer diffusion, which represents the ion's self-diffusion. It is thus useful to consider the $f$ factor:

$$f = \frac{D_e}{D}. \tag{2}$$

The $f$ factor is the inverse of the Haven ratio ($1/H_R = \sigma_{\text{ion}}/\sigma_e$) and reflects the correlation of ion association [41]. When the motions of ions are not correlated (i.e., dilute solution), charge diffusion is similar to ion diffusion ($f = 1$). When the ions are highly associated with each other, charge diffusion is smaller than ion diffusion ($f < 1$) due to the formation of neutral ion entities that have high mobility yet do not contribute to conductivity. For example, in salts dissolved in PEO systems, charge diffusion is one to two orders of magnitude smaller than ion diffusion [42–44]. All examples of superionic conductivity in amorphous ion conductors are for vitreous electrolytes, which have $f$ factors between 1.3 and 3.9 [5,9,12,45].

To determine the $f$ factor, we extract ion diffusion from the mean-squared displacement in the usual way and charge diffusion by the collective motion of ions:

$$D_e = \lim_{t\to\infty} \frac{1}{6t(N_+ + N_-)} \times \left\langle \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} z_i z_j [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \right\rangle. \tag{3}$$

Here, $i$ and $j$ refer to cations and anions, $z$ is the charge of the ion, and $\mathbf{R}$ refers to the ion coordinates. It is important to demonstrate that both the self-diffusion of Na $D$ and the collective diffusion $D_e$ have reached the diffusive limit. In Fig. 2 we consider the mean-squared displacements of Na,

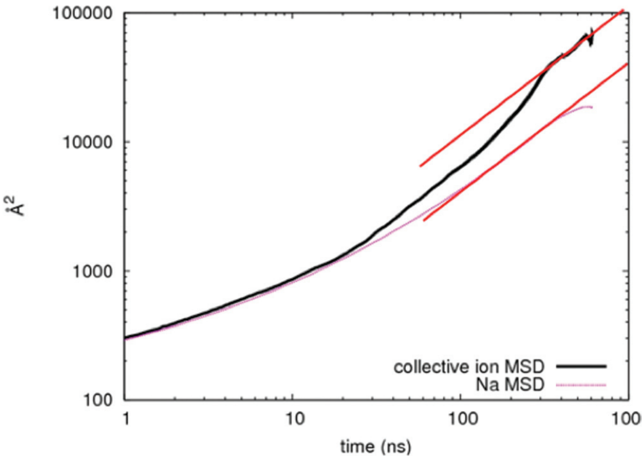

FIG. 2. (Color online) The collective ion and Na ion MSD. Red lines (two linear lines) indicate a slope of 1.

$$\left\langle \sum_{i=1}^{N_+} [\mathbf{R}_i(t) - \mathbf{R}_i(0)]^2 \right\rangle, \tag{4}$$

and collective ions,

$$\left\langle \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} z_i z_j [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \right\rangle. \tag{5}$$

Collective mean-squared displacements are rarely given, so there are few data with which to evaluate its behavior. Na ions become diffusive around 100 ns and collective ions at 300 ns. The collective mean-squared displacement changes abruptly as it becomes diffusive, which likely corresponds to the onset of specific events.

## III. RESULTS AND DISCUSSION

At $1.3T_g$, PEO600Na is superionic, with $f = 3.75$. This elastomeric superionic conductor shares characteristics with vitreous superionic conductors, specifically a large mobility difference between cations and anions and one-dimensional fast-ion streams. Cations are five times faster than anions (as assessed by ion diffusion) because the anions are incorporated in the polymer backbone, thus hindering their diffusion. On average, the ion chains have three to four cations, although chains up to eight cations are observed. The ion chains in PEO600Na are similar in length and spatial distribution to the one-dimensional streams in the superionic conductors CuI and AgI [23].

We illustrate a superionic charge transport event observed in our simulation in Fig. 3. The event utilizes chain-like aggregates as a conduction pathway: only the Na ions at either end move, with the core ions serving as the charge conduction pathway. In step 1, a Na ion moves $d_1$ to join a string-like aggregate (top image). In step 2, the Na ion at the other end moves $d_2$ to a new coordination site (bottom image). The charge transport distance, $d_1 + L + d_2$, is larger than the total ion diffusion, $d_1 + d_2$, and thus the event is superionic. This is analogous to the mechanism observed in superionic $\mathrm{LiMgSO_4F}$ [35], with the difference being that the

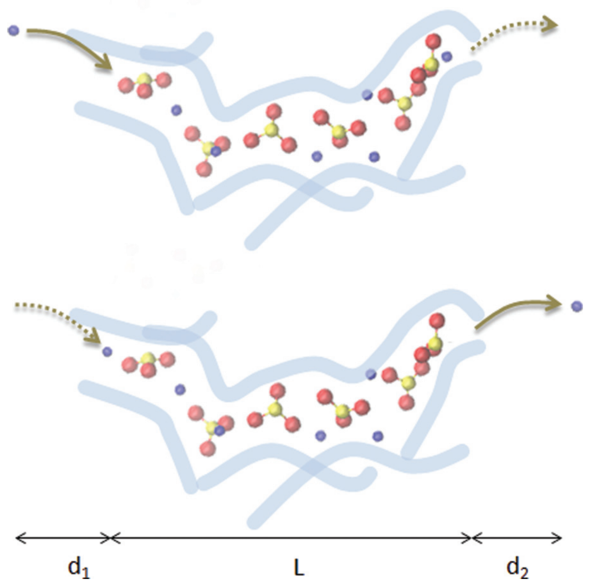

FIG. 3. (Color online) A schematic of a superionic mechanism in the PEO-based ionomer. The anions $SO_3^-$ are represented by yellow (light gray; S) and red (medium gray; O) beads. Small blue (dark gray) beads represent Na ions. A Na ion hops to an aggregate (top image), then another Na hops away (bottom image). The chain-like aggregates are surrounded by PEO segments (light blue tubes). Ion positions are taken from the MD trajectory.

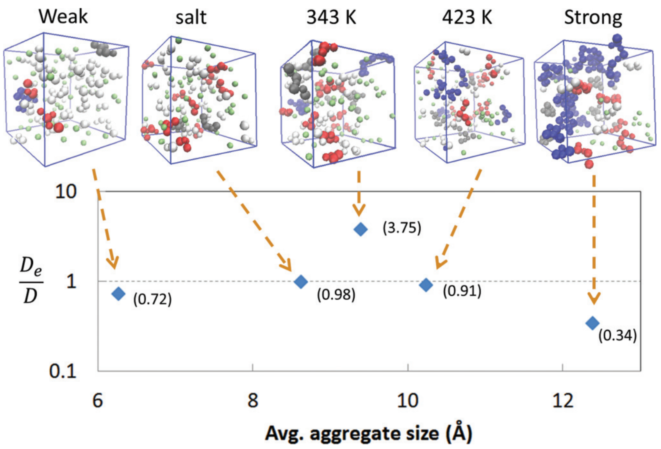

FIG. 4. (Color online) The ratio of charge diffusion to ion diffusion ($f$ factor) for various systems. All systems have the same number of ions, and the force fields and simulation details can be found in Refs. [37,38]. The $f$ factor is plotted against the size of aggregates. The average aggregate size is determined by averaging aggregates with more than three ions. Snapshots on top show cations for each system. Weak and strong models: Na-$SO_3$ interaction is weakened or strengthened compared to PEO600NA. Salt: polymer-salt configuration with the same cation-anion pair. 343 K ($1.3T_g$) and 423 K ($1.6T_g$): PEO600Na with force field tuned to experimental observables [37]. Cation states are color-coded according to size. Single cation: green. Pair and triple ions: white. Four- to six-ion complexes: red (modest). Seven- to nine-ion complexes: gray (light). Ten-ion or higher complexes: blue (darkest).

ion channels in that system contain only Li ions, whereas in PEO600Na, the ion channels contain both cations and anions. It also bears some resemblance to the Grotthuss mechanism, where a positive charge is transferred via interconversion of a hydrogen bond network of water molecules [46,47] and results in positive charge diffusion six to seven times higher than proton diffusion [48]. Following the superionic event illustrated in Fig. 3, the ion chain would need to reset itself to be used again, as the ending chain has a cation in the first position and not an anion. This occurs through diffusion of cations along the chain direction, as we observe cations moving along the chain contour but not in other directions. The cations also sometimes exchange their positions.

Interestingly, chain structures do not always lead to superionic behavior. Other PEO-based ionomers and PEO-salt systems [37–39] aggregate into chains but do not demonstrate superionic behavior [37,38]. Similarly, PEO-LiI contains ion chains but has an $f$ factor of 0.1 or smaller [49]. In Fig. 4, we investigate the correlation between the $f$ factor and the aggregate length by considering PEO600Na at $1.6T_g$, with stronger or weaker ion association imposed by varying force field parameters [39] and the same anion and cation (Na benzene sulfonate) as in a polymer-salt configuration [38]. The aggregates in all systems are one-dimensional chain-like structures, probably stabilized by stacking of the benzene rings in the anion. Superionic behavior occurs for aggregate sizes between 8.5 and 10.5 Å. Elastomeric conductors within this range have four to nine ions per chain. The small window in ions per chain arises from a balance of the number of conducting pathways and their length. All five systems have 216 ions. When the number of aggregates is large, their lengths are short. Although more aggregation pathways are present, the charge transfer distance is comparable to the Na diffusion distance. When the number of aggregates is small, the aggregate length is large. The charge diffusion distance greatly exceeds the Na diffusion distance, but few aggregation pathways present lower the probability of superionic events. We have recently completed coarse-grained simulations of the superionic system. In doing so, we found that aggregates over 10 Å (seven ions) develop curvature, with the ion chains eventually forming random walks [50]. This is evident in the strong system, where the blue (dark gray) chains are not extended, but rather begin to coil. Thus, in addition to reducing the number of chain ends, larger aggregates also reduce the charge transfer distance because they are not extended.

The two systems with aggregate lengths of 8.5 and 10.2 are almost superionic and are certainly more effective than has previously been demonstrated for an elastomeric conductor ($f = 0.1$–$0.2$) [42,44,51]. A likely reason for the less effective charge transport in these two systems is the stability of their ion pathways. The superionic mechanism proposed in Fig. 3 includes two parts, a “hop on” an aggregate, followed by a “hop off” the same aggregate. These hopping events are a collective result of polymer mobility and ion-ion association strength. In the hop-on and hop-off events, cations move a long distance (>1.5 Å) within 1-3 ps. Similar behavior was previously observed in PEO-$LiClO_4$ [52]. In order to complete a superionic transfer, the pathway must remain viable between these two events. This means that the aggregate must remain stable, with sufficient hop-on and hop-off events to drive conduction. We express this mathematically by considering

TABLE I. Probability of conduction using aggregates as pathways.

| | Salt | $1.3T_g$ | $1.6T_g$ |
|---|---|---|---|
| $P$ | 0.16 | 0.27 | 0.12 |
| $f$ | 0.98 | 3.75 | 0.91 |

the fraction of "successful hops,"

$$f_i^s = \left\langle \frac{\int_0^{\tau_{\rm agg}} P(\tau_i)d\tau_i}{\int_0^{\infty} P(\tau_i)d\tau_i} \right\rangle_{\rm agg}, \tag{6}$$

where we define "successful" as a hop that occurs before the aggregate disassembles. This fraction compares the system ensemble averaged hop-on or hop-off time $\tau_i$ with the lifetime of each aggregate (equal to or greater than three ions) formed during the simulation. The ensemble average over all aggregates is taken at the end. A superionic event requires both events to take place, and thus its probability is proportional to the product of successful hop-on and hop-off fractions:

$$P \propto f_{\rm on}^s f_{\rm off}^s. \tag{7}$$

As demonstrated in Table I and anticipated above, the conducting aggregates in the superionic conductor have close to twice the chance to complete a superionic event before they disassemble. Aggregate stability arises from temperature and the strength of anion-cation interactions. Only the ion interaction strength is connected to aggregate size, and thus it should be possible to control aggregate stability by adjusting temperature, as in the $1.3T_g$ and $1.6T_g$ simulations of the same system. Stabilizing the aggregate would require a temperature *decrease*, whereas the normal attempt to improve conductivity would be to *increase* the temperature.

In summary, we observe superionic behavior in an elastomeric conductor. This elastomeric superionic conductor shares features with vitreous superionic conductors, such as chain-like ion configurations and a large difference between the mobility of cations and anions. Superionic behavior is achieved by stable, string-like aggregates between 8.5 and 10 Å (four to seven ions). Because the best way to increase aggregate stability is to reduce ion motion by decreasing temperature, it suggests a counterintuitive way to improve the efficiency of conduction and the possibility of level conductivity over a wide temperature range. Superionic conduction reduces dependence on polymer mobility, thus allowing for conductivity while improving mechanical strength.

## IV. CONCLUDING REMARKS

The superionic material described here has been the subject of laboratory experiments as part of a series of Li, Cs, and Na single-ion conductors [36,53–61]. Because the ion aggregates have nontraditional shapes, small angle x-ray scattering is not sufficient to determine aggregate size and orientation. It would be useful to perform Na NMR, so that cation diffusion can be assessed and compared to charge diffusion from conductivity. Conductivity (charge diffusion) is not sensitive to the level of aggregation, which varies widely over the 10–15 PEO single-ion conductors studied so far [36–39,53–61]. This suggests that some of these single-ion conductors utilize superionic mechanisms. Given the small range of aggregate lengths and the dynamic balance required to achieve superionic conductivity, MD is a crucial guide towards experimental verification of superionic conduction in elastomers.

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