Molecular dynamics study of a dual-cation ionomer electrolyte

This is the accepted manuscript.

This is the peer reviewed version of the following article:


which has been published in final form at http://www.dx.doi.org/10.1002/cphc.201600821.

This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

© 2016, Wiley-VCH

Downloaded from DRO:
http://hdl.handle.net/10536/DRO/DU:30086365
Molecular Dynamics Study of a Dual-cation Ionomer Electrolyte

Xingyu Chen[a], Fangfang Chen[a], Erlendur Jónsson[a][b], Maria Forsyth[a][b]

Abstract: The poly(N_{1220},Li,x)[AMPS] ionomer system with dual cations has previously shown decoupled Li ion dynamics from polymer segmental motions, characterized by the glass transition temperature, which can result in a conductive electrolyte material whilst retaining an appropriate modulus (ie. stiffness) so that it can suppress dendrite formation, thereby improving safety when used in lithium metal batteries. To understand this ion dynamics behavior, molecular dynamics techniques have been used in this work to simulate structure and dynamics in these materials. These simulations confirm that the Li ion transport is decoupled from the polymer particularly at intermediate N_{1220} concentrations. At 50 mol% N_{1220} concentration the polymer backbone is more rigid than for higher N_{1220} concentrations, but with increasing temperature Li ion dynamics is more significant than polymer or quaternary ammonium cation motions. Here we suggest an ion hopping mechanism for Li\textsuperscript+ arising from structural rearrangement of ionic clusters that could explain its decoupled behavior. Higher temperatures favor an aggregated ionic structure as well as enhancing these hopping motions. The simulations discussed here provide an atomic-level understanding of ion dynamics that could contribute to designing an improved ionomer with fast ion transport and mechanical robustness.

Introduction

Polymer electrolytes are of great interest for lithium secondary battery applications due to their flexibility, inherent safety and low flammability\cite{1}. Despite these advantages over liquid electrolytes, a major problem facing polymer electrolytes is that the mobile anions tend to accumulate at the electrode/electrolyte interface after several charge/discharge cycles. Such a problem is known as concentration polarization\cite{2,3} that could lead to reduced battery life or complete failure of electronic devices. To circumvent this problem, several approaches exist to reduce the mobility of anions including the adoption of heavy anions or immobilization of anions\cite{4,5}. The latter method generates a class of polymeric electrolytes called polyelectrolytes.

Polyelectrolytes are a class of ionomers that tether anions to a polymer backbone and thus only allow the cations to conduct. While immobilizing the anions is successful in addressing the polarization issue, a major shortcoming of polyelectrolyte is its low ionic conductivity. As the anions are attached to the polymer backbone, the ionic interaction between immobilized anions and cations generally leads to the formation of ion aggregates and ionic crosslinks between chains, that would considerably restrict the mobility of polymer segments, thereby resulting in high glass transition temperatures (T_g)\cite{6}. It is well documented in traditional polymer/salt systems that the reduced polymer mobility has a negative impact on ion conductivities because the ion transport mechanism relies on the cooperative movement with polymer segments.

One of the successful approaches to improve ionic conductivity is to employ a charge-delocalized cation. Colby et al. found that the bulky cationic counterions, such as ammonium-based, phosphonium-based and imidazolium-based cations, work as plasticizers in ionomers and improve the ionic conductivity significantly\cite{7,8}. Recently, our group also investigated some dual cation polyelectrolytes containing the ammonium-based cations with either the Li\textsuperscript+ or Na\textsuperscript+ co-cations. The ionic conductivity was found to increase when the ratio of the organic cations increased and, more importantly, the results suggested that the alkali cation dynamics were decoupled from the polymer’s T_g in these systems, which means the ionic conductivity did not drop significantly upon decreasing the temperature below T_g. These results may indicate a change in the transport mechanism of the alkali ions in these dual cation ionomer systems in the presence of the organic cations.

Although these promising results have been obtained through experimental investigations, Nuclear Magnetic Resonance measurements confirmed the Li ion motion was decoupled from T_g\cite{14,16} addressing the ion transport mechanism in these polymer systems is still difficult due to the complexity of the structure and dynamics involved. An in-depth understanding of the decoupled behavior at the atomic-level is essential for designing polyelectrolytes that could combine mechanical robustness and sufficient ionic conductivity. Furthermore, understanding the optimum composition and chemical structures that could enhance conductivity and decoupling behaviors would require a multitude of time consuming experimental parameters to be explored. Hence, molecular modeling techniques are an ideal way to delve more deeply into understanding the ion dynamics and their relationship to structure and composition. Such techniques have already provided useful insights in recent studies. For example, modeling methods have been applied to investigate the ion transport in traditional polymer/salt systems\cite{17-22} and mixture of ionic liquids and polymer electrolytes\cite{23,24}, however, these methods are still investigated less in the dry ionomers\cite{25-28}. A recent molecular dynamics (MD) study\cite{27} has compared a Na\textsuperscript+ conducting polyester-sulfonate ionomer with its corresponding PEO/Na(5-sulfosulfonato) salt system. It was shown that the dynamics of the polymer matrix controls the ion transport in PEO/salt system, whereas the ion hopping mechanism dominates in the rigid ionomer system which relies on a change of the local coordination states. Another MD study\cite{28} based on a coarse-grained ionomer model showed that the transport of the counterions depends on the breaking and formation of ion clusters, i.e. the counterion can move without leaving its aggregation environment. This simulation might be non-ergodic, as it did not catch the process of any Li ion leaving its aggregate. These previous studies investigated the ion transport mechanism and the ion dynamics at the atomic level in ionomer models. In this work, to the best of our knowledge, we present for the first time, a molecular
dynamics study on a dual-cation ionomer system. This work focuses on the theoretical investigation of the ion dynamics and the decoupling behavior, which has been experimentally suggested to occur, in a dual-cation ionomer: poly(N_{1222})_{1-x}Li_{x}[(AMPS)_{y} ((N_{1222})_{1-x}Li_{x}PAMPS) (0 < x < 1)^{14,15}](Scheme 1). We are particularly interested in the effect of ammonium co-cation on the Li ion dynamics.

Scheme 1. Chemical structure of (N_{1222})_{1-x}Li_{x}PAMPS

Results and Discussion

Structural Analysis

The arrangements of the cations, especially the Li⁺, and the ionomers were investigated by calculating the radial distribution function (RDF) between two atoms. An RDF describes the probability of finding a particle B from a given particle A as a function of distance. In Figure 1 the RDFs of Li-O_{sulfonate}, Li-O_{carbonate}, Li-S, and S-N_{ammonium} were generated for two polymer systems consisting of either the 50% or 80% N_{1222} cation at 393 and 343 K, respectively. In all simulation systems, the first prominent Li-O_{sulfonate} and Li-O_{carbonate} RDF peaks are shown at the same position of around 2.1 Å, which demonstrates that the first coordination shell of the Li⁺ consists of oxygen atoms not only from the sulfonate but also from the carbonate groups. For 50% ammonium systems (Figure 1(b)), the coordination number (CN) of the oxygen atoms calculated from this peak shows that the sulfonate oxygen atoms are dominant in the first coordination shell with a CN of about 4.3 (blue curve); the CN of the carbonate oxygen is only around 0.6 (orange curve). The second Li-O_{sulfonate} peak at around 4.4 Å is attributed to the remaining oxygen atoms from the SO_{2}⁻ groups, but these fall into the second coordination shell of Li⁺. Moreover, the first RDF peak of Li-O_{sulfonate} is broader than that of Li-O_{carbonate} because there are various possible coordination geometries between the Li and the SO_{2}⁻ group, which also lead to two overlapped peaks between 2 and 4 Å in the Li-S RDFs. Two typical coordination geometries between Li and two O atoms gives the shorter Li-S distance (2.984 Å in snapshot) that contributes to the first Li-S RDF peak; whereas the mono-dentate geometry has the longer Li-S distance of more than 3 Å (3.46 Å in this case) and results in the second Li-S RDF peak.

Figure 1. Radial distribution functions between different atoms for (a) 50% and (c) 80% ammonium systems at both 343 and 393 K. The coordination number profiles were calculated from the RDFs at 393 K for (b) 50% and (d) 80% ammonium systems.

The structure arrangement between the ammonium cation and the sulfonate was also investigated through calculating RDF between the N atom in the ammonium and the S atom in the sulfonate in both 50% and 80% ammonium systems. One board N-S RDF peak appears at around 5.2 Å in both Figure 1 (a) and (c) with the distinctly larger CN in 50% ammonium system. It is clear that, compared to the Li-S distance, the N atom in ammonium is much further from the S atom, which is due to the steric hindrance of the bulky ammonium cation^{110}.

Figure 2. A snapshot from simulation shows both bi-dentate (left) and mono-dentate (right) coordination geometries between Li⁺ and SO₂⁻.

Temperature shows a negligible effect on all RDF peaks and their CNs. For example, when temperature is decreased from 393 K to 343 K, the CNs of Li⁺ and sulfur are essentially unchanged. However the N_{1222} concentration slightly changes the RDF peaks and their CNs. When it increases from 50% to
80%, the Li-O CN slightly decreases from 4.3 to 4.2 for O$_{sulfonate}$, but increases from 0.6 to 0.7 for O$_{carbonate}$, and this makes the total CN with oxygen unchanged. RDF plots only calculated structures between neighbouring ions; in addition, we also studied the distribution and connectivity of Li-anion aggregates in two ammonium systems. The aggregates were decided by calculating distance between neighbouring Li and S (SO$_3^-$). If the distance is less than a cutoff of 4 Å, which is the first minimum after the first peak in Li-S RDF, these neighbouring ions are believed to be in the same aggregate. All the Li$^+$ cations coordinating with the same sulfonate anions are also considered to be in the same aggregate. The ions in the same aggregate are given the same colour. Figure 3 illustrates these aggregates at 343 K in two systems. It is clearly seen in the 50% ammonium system that the Li ions and the coordinated sulfonate groups form the larger or even percolated aggregates that span the simulation box, and apparently ion aggregates become smaller and discrete when the ammonium concentration increases to 80% and the Li$^+$ concentration decreases to 20%. These suggest that including the large amount of the N$_{1222}^-$ cations in the lithium ionomers can effectively inhibit the formation of the large Li-anion aggregates.

![Figure 3. Li-S aggregates calculated in both (a) 50% and (b) 80% ammonium systems at 343 K. Ions with the same colour belong to the same aggregate. Here only Li$^+$ and S in SO$_3^-$ were displayed.](image)

Dynamics Analysis

Mean square displacement (MSD) data provide information on the average displacement of a particular atom as a function of time, and was calculated here to study the diffusion of the various ions. Figure 4 gives the MSD data of four different atoms: Li$^+$, N atoms in N$_{1222}$, S atoms in the tethered sulfonate groups and C atoms in the polymer backbone. Here we investigate the effect on polymer dynamics for both the temperature and ammonium counterion concentration. Obviously, the increased temperature helps to improve the dynamics of both ionomer segments and the cations, leading to an increase in all MSD trajectories calculated. Such an increase is particularly pronounced for the Li ion and in particular for the 50% system. This is consistent with the solid state $^7$Li nuclear magnetic resonance studies, which indicate that line narrowing for $^7$Li begins below T$_g$, a clear evidence for a decoupling of Li motion from the polymer segmental mobility\cite{14}.

Concentration shows a prominent effect on dynamics of both ionomer and cations. An improvement in polymer dynamics is observed as the concentration of N$_{1222}^-$ increases from 50% to 80%, reflected from both the sulfonate chains and backbone, consistent with a lower T$_g$ with increasing ammonium cation concentration\cite{14}. MSDs of S and C in Figure 4 (a) and (b) both increase in the higher N$_{1222}^-$ concentration system at all temperatures. In contrast, the ionomer motion is very slow in a 80% system with a relatively flat MSDs for both S and C even the temperature is at 393 K (T$_g$ for this system is 441 K\cite{16} and thus we are well below T$_g$ in these simulations). For example, the S MSD merely reaches 4.5 Å$^2$ and the C MSD reaches 3 Å$^2$ after 10 ns. In comparison, it is improved in an 80% system and the MSD of C atom could reach 8 Å$^2$ at 393 K (close to the expected experimental T$_g$) after 10 ns. Similar changes in dynamics are also observed for the ammonium cation of which the MSDs reach higher values after 10 ns in the 80% N$_{1222}^-$ concentration system (Figure 4 (c)). In the experimental reports, the improvement in dynamics are associated with the lower T$_g$, which can be further explained from structure changes in Li-anion aggregates (as seen in Figure 3) through MD simulations; fewer physical cross-links exist with the addition of more N$_{1222}$ cations which lowers the T$_g$ and thus enhances the polymer dynamics. These are also supported by an ab initio study\cite{11} which has shown that the bulky ammonium cations associate less with polymer side chains, resulting in less physical cross-links. Because of this, N$_{1222}$ cations and sulfonate groups (N and S MSDs) are more active in 80% systems whereas the N$_{1222}$ cations in 50% systems are rather sluggish, and similar as for the polymer backbone atoms.

Interestingly, in contrast to the ionomer and ammonium cation dynamics, the Li ion dynamics do not favor such a change in structure; the increased ammonium concentration shows less effect on Li$^+$ and even a slight lowered MSD after 10 ns is observed at each temperature in Figure 4(d). In other words, the increased polymer mobility resulting from the higher ammonium...
concentration does not bring about a corresponding enhancement in Li ion dynamics. The Li ion dynamics seem to favor a greater degree of aggregation. However, here the temperature also plays another important role in the 80% N$_{1225}$ system, although Li ions are slower than N$_{1222}$ cations at 343 and 373 K, their MSDs finally exceed those of the ammonium cations at 393 K, indicating that Li$^+$-containing anionic ionic species show more conductivity as the temperature increases due to a local change in configuration approached in this system (around 390 K)\cite{10}. Moreover, in the 50% ammonium system where the ionomer is relatively rigid at the simulated temperatures that are well below $T_g$, the increased temperature only slightly increases the dynamics of the polymer and the N$_{1222}$ Cations, whereas it significantly enhances the Li ion dynamics and makes it the fastest ion compared with the other charged components. This indicates that the Li ions are the dominant charge carrier in this rigid ionomer system and is consistent with the decoupling we have observed experimentally, where significant conductivity ($>10^{-4}$ S/cm) and line narrowing is measured in this ionomer composition well below $T_g$\cite{10}. These observations indicate that the main diffusion mechanism of the Li ions here does not largely rely on the segment movement of the ionomer but is more likely to be an independent ‘hopping’ mechanism. The van Hove self-correlation function was calculated to investigate the hopping of the Li ions. The van Hove correlation function is defined as $G_r (r, t) = \sum_i \delta (r - r_i(t) + r_i(0))/N$, where the $r_i(t)$ is a time dependent position coordinate. In an isotropic system, $4\pi r^2 G_r (r, t)$ describes the probability that a particle moves a distance $r$ within a time $t$. Thus, a shifting of the peak with time is a signal of the translational motion of the selected particles and appearance of a second or additional peaks indicates the hopping of the particles to new sites. This function was calculated for Li ions in both the 50% and 80% systems at two different temperatures of 343 K and 393 K in Figure 5. At each temperature, the $4\pi r^2 G_r (r, t)$ was produced at five different time points of 500 ps, 2.5 ns, 5 ns, 7.5 ns and 10 ns to illustrate the changes of the function with time. In a 50% N$_{1225}$ concentration system, the hopping of Li ions is clearly seen at both 343 and 393 K. At 343 K in Figure 5(a), the second peak already appears at 500 ps but grows slowly with time. Although the first peak becomes slightly broader, this function basically does not change much throughout 10 ns, which indicates that these Li ions are mainly trapped at their sites but some are able to hop to nearby sites. As the temperature increases to 393 K in Figure 5(b), the shape of this function changes dramatically with time; the first peak becomes much broader, the second peak grows significantly after 2.5 ns and we see the appearance of a third peak. All these changes suggest a hopping diffusion mechanism of the Li ions is present in these systems. However, as the ammonium concentration increases to 80%, it is shown in Figure 5(c) that the Li ions are completely trapped throughout the 10 ns without any hopping at 343 K and the hopping diffusion needs a higher temperature to be stimulated. All these results are consistent with the MSD analysis. The Li ion behavior at a lower temperature (below the ionomer $T_g$) could suggest the importance of its local structure on its dynamics. It is evident that in a system with a high concentration of Li$^+$, larger Li-anion clusters are more likely, and this appears to favor facile Li ion dynamics through providing more equivalent sites for Li ions to hop via a structural rearrangement mechanism. Such a mechanism has also been reported in some high Li concentration ionic liquids, in which the aggregation structure also facilitates the movement of the Li ions and leads to the high Li transference number\cite{20,21}. As the addition of the ammonium inhibits the formation of ionic aggregates, Li ion hopping becomes more difficult at low temperatures, and then the Li ion motion relies more on significant dynamics of the ionomer itself.

Although the visualization in Figure 3 displays the distribution and connectivity of ion aggregates, there could be a great variety of Li$^+$ cation states, i.e. different sized local Li clusters, existing in the simulation systems that exert different influence on Li ion dynamics. We define the cation states by counting the average number of neighboring Li ions for each Li ion within a cut-off distance through the entire trajectory. The cut-off distance is determined by the first minimum value between the first and second peak in the Li-Li RDF plot. Therefore, Li cation states can be categorized into single ions ($N<0.4$), ion pairs ($0.4≤N<1.4$), triple ions ($1.4≤N<2.4$), quadratic ions ($2.4≤N<3.4$) and multiple ions ($N≥3.4$), where $N$ is the average number of the neighboring Li$^+$ cations. To look at the dependence of dynamics of each Li ion on its cation states, the individual Li ion dynamics was then examined using its MSD value at the end of 10 ns so that the fastest and the slowest 10% Li ions were sorted into the cation state to which they belong. These results were presented in Figure 6.

The percentages of the Li ions in each of five cation states were calculated separately on 10% fastest ones, 10% slowest ones and all Li ions. The distribution of these ions in each state are affected significantly by ammonium concentration. In 80% ammonium systems, the Li ions mainly fall into the first four categories but with very few ions falling into the large-size category, and none are in the “multiple” category. The majority of ions are either in a pair or in a triple state. In contrast, the predominant form of cation state in 50% systems is “multiple”, which comprises over 40% of the total Li ions. These results confirm the effect of the ammonium concentration on this material structures. The statistics on the fastest and slowest Li ions reveal the correlation between the Li cation states and Li ion dynamics. The majority of the fastest Li ions favor a cluster environment, and this is more evident in the high Li concentration systems. In the 50% Li system, there are 60-80% fastest Li ions falling into the “multiple” category. In 20% Li systems, the fastest ions are still more likely to appear in the ion pairs or triple-ion clusters rather than in the single state. On the other hand, there is no clear pattern that the slowest ions would
favor a particular ion state. The distribution of these slowest ions varies in different cases.

![Image of percentages of Li ions in each of five states in two systems at three different temperatures]  
**Figure 6.** Percentages of the Li ions in each of the five states in two systems at three different temperatures. The statistics were made on 10% fastest, 10% slowest and all Li ions separately.

Presumably, the decoupling behavior in these polymer systems might arise from the ion hopping of fast Li\(^+\) within large Li–anion clusters. The ion states, which is significantly affected by the concentration of the organic co-cations, play a key factor for ion hopping here. Ion hopping is more likely to occur in extended ion aggregates that consist of a greater number of large ion clusters whereas those single Li ions tend to be confined to their local coordinating environment. This result is different from a previous MD study on Na\(^+\)-based polyester-sulfonate ionomers\(^{[26]}\), in which the diffusion of the Na ion was affected more by polymer backbone movement due to the coordination to the ether oxygen on backbones.

**Conclusions**

In this work, we studied the effect of co-cation concentration on the Li ion dynamics in the dual cation ionomer, poly(N\(_{122}(x)\)-Li\(_{1-x}\)) PAMPS. This study successfully disclosed the decoupled behaviour of the Li\(^+\) from polymer dynamics, which has been observed in experimental investigations. The concentration of the co-cation N\(_{122}^+\) shows the impact on the structure of the system, altering the local environment of the Li ions which in turn affects Li ion dynamics. The increased number of ammonium cations reduces the cross-links in the material and effectively increases polymer dynamics as reflected in the lower \(T_g\) polymer. However, the “softened” polymer does not necessarily lead to fast Li ion dynamics. On the other hand, the Li ion dynamics is apparently higher than the polymer dynamics in a 50\% Li concentration system. These all support that Li mobility is decoupled from the polymer mobility. This could be attributed to the ion hopping events, which do not rely on the segmental motion of polymer. These hopping events are mainly affected by temperature and the size of local Li clusters. Either increased temperature or extended ion clustering could facilitate the ion hopping process. Therefore, Li ion dynamics at low ammonium concentration systems are comparable to, or even higher than, those for higher ammonium ion concentrations even though the latter are themselves intrinsically more mobile. As the extended ion aggregates enhance the chance of ion hopping and consequently lead to decoupling behaviour, it would be possible to design a mechanically robust yet sufficiently conductive dual-cation ionomer. Future work will explore in more detail the composition and chemical structure of such ionomers to determine if this analysis could lead to a predictive approach to solid electrolyte design.

**Simulation Section**

Two dual-cation ionomer systems of N\(_{122}(x)\)-Li\(_{1-x}\) PAMPS (Scheme 1) consisting of 50\% (x=0.5) and 80\% (x=0.8) N\(_{122}\) cations, respectively, have been investigated at three temperatures of 343 K, 373 K and 393 K using molecular dynamics techniques. The force field parameters for the PAMPS and Li\(^+\) cation were directly taken from the general Amber force field (GAFF\(^{[27]}\)). The force field parameters of the ammonium were taken from Liu et al\(^{[28]}\) in which the parameters of ammonium were fitted in the GAFF format, which is shown in Eq.1.

\[
\nu_{\text{total}} = \sum K_r (r - r_{eq})^2 + \sum K_{\theta} (\theta - \theta_{eq})^2 + \sum \frac{K_{\phi}}{2} [1 + \cos(n\phi - \gamma)] + \sum_{i<j} \left( \frac{\alpha_{i,j}}{r_{ij}^{12}} - \frac{\beta_{i,j}}{r_{ij}^6} + \frac{\epsilon_{i,j}}{r_{ij}^{12}} \right)
\]

Eq. 1

Here, the total energy consists of four terms: bond stretching, angle bending, dihedral torsion, improper dihedral torsion, and van der Waals and electrostatic interactions. The Lorentz–Berthelot combining rules were used to handle the van der Waals parameters for unlike atoms. The partial atomic charges were calculated by the restrained electrostatic potential (RESP) method\(^{[29]}\) using the Density Functional Theory (DFT). A single repeat unit of PAMPS was optimized at B3LYP/6-31+G\(^*\) level of theory using the Gaussian 09 package\(^{[30]}\). Net charges of –1 were assigned to the AMPS repeat unit. Here, a reduced charge method was adopted due to two reasons; first, the ionic net charges would be lower than the full charges in the ion–ion interaction due to the polarizability of the molecule; second, applying a polarizable force field to the simulation of an ionomer is unrealistic because of the significant simulation time required and the lack of accurate polarizable potential functions. Several simulations on polyelectrolytes have employed the reduced charge model in which the partial charges are typically scaled down to about 0.5-0.56\(^{[18, 19, 20]}\). In our study, we have attempted several scale factors between 0.5 and 0.8. Due to the sluggish ion dynamics and prohibitive computational time, we arrived at the conclusion that a smaller scale factor can facilitate ion dynamics and save CPU time, yet allow a study of the effect of compositional changes on the behaviour of these systems. We stress this was not a random choice as it is very common to use 0.5 in such systems. However, the use of 0.5 scale charge rendered an
unrealistic fast ion dynamics within a short simulation time. Since our study focuses on the qualitative analysis of two cation concentration systems, we arrived at a 0.6 scale factor. When compared to the 0.7 scaled charges, our systems increased the ion-ion interaction distance and decreased the size of ion aggregates.

We applied Monte Carlo simulations to generate the initial polymer conformers in a cubic simulation box with the periodic boundary condition on all directions. The simulation box consists of 16 polymer molecules and each molecule has 12 repeat units, 50% and 80% ammonium systems have 96 Li/NH$_2$N$_{1222}$ and 38 Li/NH$_2$N$_{1222}$, respectively. The Monte Carlo simulation is carried out using Amorphous Cell module in Materials Studio[39]. The polymer conformers were further optimized to be used as the initial structures for MD simulations. These structures were equilibrated at 393 K first using the NPT ensemble with the Nosé-Hoover thermostat and barostat. The optimal relaxation times for the thermostat and the barostat were 1.0 ps and 5.0 ps respectively. The systems were then cooled down and equilibrated at 373 K and 343 K, respectively. The structural property at each temperature was calculated based on a 500 ps production run after equilibration. The algorithm to compute the equation of motion uses Verlet integration with a time step of 1.0 fs. The long-range electrostatic interactions were treated by the standard Ewald summation method with accuracy of 1×10$^{-6}$ and a cut-off of 12.5 Å. The dynamics calculations were conducted using the NVT ensemble for 15 ps and a cut-off of 5.0 ps at each temperature. All MD simulations were conducted using the DL_POLY classic program[39]. Some analysis employed the MDAnalysis software package[39].

Acknowledgements

The authors appreciate the financial support under FL110100013 from Australian Research Council (ARC). The authors also thank the National Computational Merit Allocation Scheme of “Rajin” for the computational resources.

Keywords: ion dynamics • ionomer • polymer electrolyte • Li ion battery • molecular dynamics simulation

34. Frisch, M.J., et al., *Gaussian 09 Revision E.01*, 2009, Gaussian, Inc.: Wallingford, CT, USA.


Molecular dynamics simulations were carried out to study structure and dynamics in a dual-cation ionomer with different \( N_{1222} \) co-cation concentration. These simulations confirm that the Li ion transport is decoupled from the polymer particularly at intermediate \( N_{1222} \) concentrations with ion hopping for Li\(^+\), arising from structural rearrangement of ionic clusters.