

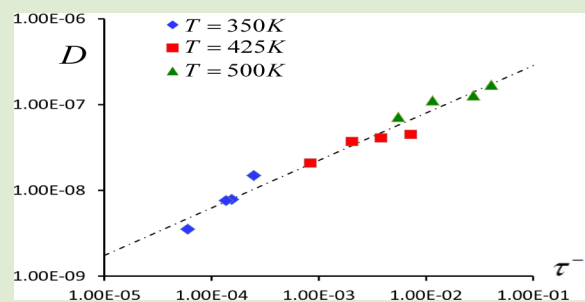
Mechanisms Underlying Ionic Mobilities in Nanocomposite Polymer Electrolytes

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S Supporting Information

ABSTRACT: Recently, a number of experiments have demonstrated that addition of ceramics with nanoscale dimensions can lead to substantial improvements in the low-temperature conductivity of the polymeric materials. However, the origin of such behaviors and, more generally, the manner by which nanoscale fillers impact the ion mobilities remain unresolved. In this communication, we report the results of atomistic molecular dynamics simulations which used multibody polarizable force fields to study lithium ion diffusivities in an amorphous poly(ethylene-oxide) (PEO) melt containing well-dispersed TiO₂ nanoparticles. We observed that the lithium ion diffusivities decrease with increased particle loading. Our analysis suggests that the ion mobilities are correlated to the nanoparticle-induced changes in the polymer segmental dynamics. Interestingly, the changes in polymer segmental dynamics were seen to be related to the nanoparticle's influence on the polymer conformational features. Overall, our results indicate that addition of nanoparticle fillers modifies polymer conformations and the polymer segmental dynamics and thereby influence the ion mobilities of polymer electrolytes.



Electrochemical devices such as batteries and fuel cells have recently become popular in the quest for clean and sustainable energy sources. Electrolytes that facilitate ion transport between electrodes are key components in such devices, and polymeric membrane materials have emerged as attractive candidates for such applications.^{1–6,6–12} However, high ionic conductivities in polymeric materials are often obtained in rubbery polymers which lack the requisite mechanical strength for solid state batteries.¹³ In an effort to enhance the mechanical properties of such polymer membranes, a variety of strategies have been explored, such as cross-linking of the conductive homopolymers, using diblock copolymers, etc.^{14–23} In such contexts, interest has recently arisen in the strategy of using “nanocomposite” membranes, which contain nanoscale inorganic fillers dispersed in the polymer matrix.^{24–31} A number of studies have demonstrated that the addition of ceramic particles having nanoscale dimensions and suitable surface characteristics can improve properties such as anodic stability,²⁹ the low-temperature conductivity, and the cyclability of the polymer matrix.^{32–36} Such demonstrations have provided a strong motivation for understanding of the influence of nanoparticles on the electrochemical properties of polymeric electrolytes.

This specific work is motivated by the influence of nanoscopic filler particles upon the low-temperature conductivity of the polymer matrix. For instance, Croce et al.²⁷ considered TiO₂ particles dispersed in a poly(ethylene-oxide) (PEO) matrix and demonstrated an increased ionic conductivity relative to the pure polymer matrix. Such results were rationalized by suggesting that the addition of nanoparticles suppresses the crystallization of the polymer matrix to promote

the local mobility of the polymers.^{29,37,38} On the other hand, some experiments have noted that conductivity enhancements in composite polymer electrolytes can occur even at temperatures above the melting point of the polymer, which suggests that the physical mechanism underlying conductivity enhancements cannot be attributed solely to the suppression of crystallization.^{25,29,39,40} Moreover, in some cases, lowering of conductivity has been observed upon the addition of nanoparticle fillers.^{37,41} Such contradicting results motivate the questions, “What are the mechanisms underlying the ionic conductivities of polymer nanocomposites?”, “Do ion conductivities in polymer nanocomposites always correlate with the influence of the fillers on the polymer mobilities?”, and “What is the role of nanoparticle-induced modifications in polymer conformations in influencing ion mobilities?”

Atomistic molecular dynamics based on polarizable force fields remain the most accurate means to explore transport mechanisms of solid polymer electrolytes in computer simulations.^{42–51} However, due to the extremely low values of the diffusion coefficients of the ions and the multibody nature of the force fields, such simulations are computationally expensive. To overcome such computational limitations, we have recently adapted the methodology proposed by Neyertz et al.,^{52,53} which utilizes a combination of molecular dynamics and trajectory-extending kinetic Monte Carlo (TEKMC) simulations. In brief, the methodology begins with well-equilibrated

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atomistic configurations of the polymer membrane system and a specified concentration of penetrants. A fictitious rectangular grid is superimposed on the atomistic simulations to serve as the lattice framework for KMC simulations. The penetrant motions are tracked using atomistic simulations and are used to populate a matrix of residence time distributions and transition rates for the lattice grid. The construction of such a transition matrix only requires the atomistic simulations to be effected to the extent that the different diffusion paths of the penetrants create continuous, percolating paths through the simulation box.^{52,53} Typically, the time required to satisfy such a constraint is much shorter than the time required to achieve the asymptotic linear mean-squared displacement regime of the ions (but is longer than the segmental relaxation times of the polymer and therefore allows us to capture the hopping motion characteristic of ion diffusion in polymers).⁵² The transition probability matrix generated during the atomistic simulations is then used as the basis for lattice kinetic Monte Carlo simulations of a freely moving penetrant on the lattice grid with specified transition rates and occupation probabilities. Such coarse-grained simulations are then used to probe the long time dynamics of ions and their diffusivities.

Our atomistic MD simulations were performed for a melt of 40 chains of polyethylene oxide of 54 repeat units, with LiBF₄ salt at ratios of ether oxygen to Li ions of 15:1 and 8:1. Systems with TiO₂ nanoparticle weight percentages of 5, 10, and 20% were created. Simulations were performed in the NPT ensemble at 1 atm and temperatures in the range 350–500 K. Further details of the atomistic simulations, the setup, force fields, and the equilibration protocols etc. are presented in the Supporting Information. We note that the previous applications of TEKMC methodologies have primarily been concerned with the transport of small-molecule gaseous penetrants.^{52,53} As evidence of the applicability of the TEKMC framework, in the Supporting Information we present a comparison between the ionic mean-squared displacements deduced by TEKMC methodologies and more detailed atomistic simulations. Moreover, using atomistic simulations Borodin et al.⁵⁴ reported a Li ion diffusivity of 1.1×10^{-7} and 6.0×10^{-8} cm² s⁻¹, respectively, for the pure PEO and 10 wt % nanocomposite at a salt loading of 15:1 and 423 K. Our TEKMC method predicts diffusivities of 1.63×10^{-7} and 7.41×10^{-8} cm² s⁻¹, respectively, for the same salt loadings at 425 K. These numbers can be considered as comparable (within the typical errors involved in extracting diffusivities from the slopes of displacements) and serve to validate the TEKMC procedure used in this article.

In Figure 1, we present results for the lithium ion diffusivities, D , in PEO matrices as a function of particle loading for three different temperatures. We observe that there is a monotonic increase in the ion mobilities with increasing system temperature. Such a behavior can be understood as a consequence of the increase in polymer mobilities with increasing temperature. More pertinently, we observe that at a specified temperature the lithium diffusivity decreases monotonically with the addition of nanoparticles. We note that in general the addition of nonconducting nanoparticle obstacles is expected to block conducting pathways and lead to diminished ion diffusivities. However, the mobility reductions expected from such effects are expected to be less than 10% for even the highest particle volume fraction considered in our study (which was of the order of 5%). It can be seen that the mobility reductions in our system significantly exceed the magnitudes expected from such

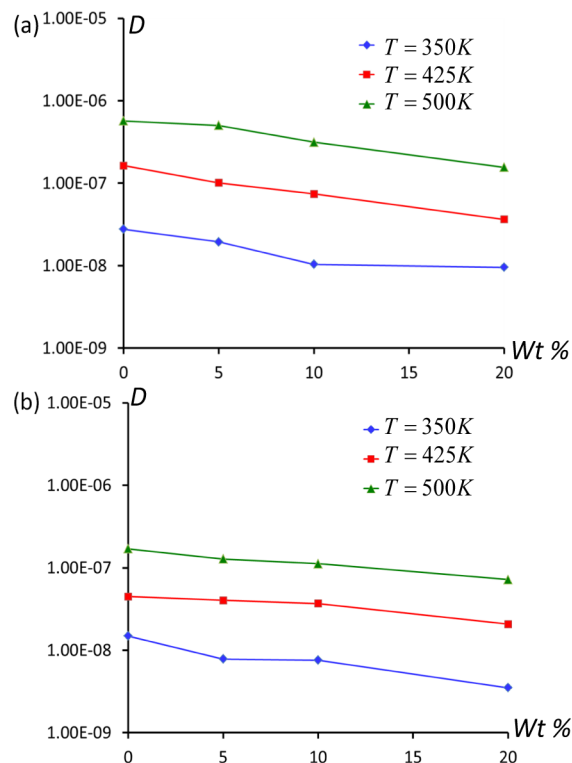


Figure 1. Diffusivities D (cm² s⁻¹) of lithium ions in PEO + TiO₂ nanoparticle matrices as a function of weight percentage of nanoparticles: (a) EO:Li = 15:1 and (b) EO:Li = 8:1. Lines are meant to be a guide to the eye.

obstructional effects and indicate nontrivial mechanisms underlying the influence of nanoparticles.

To unravel the origin of the behaviors seen in Figure 1, we probed the influence of the nanoparticle upon the polymer segmental mobilities. Toward this objective, we quantified the segmental relaxation dynamics of the PEO using the time dependence of the autocorrelation function of dihedral angles in the PEO chains. Figure 2 displays the mean segmental relaxation times τ deduced by fitting such results to a stretched exponential fit (the dynamical relaxation curves are presented in the Supporting Information). It can be observed that in all cases the relaxation of the segmental dynamics becomes retarded with the addition of nanoparticles. Moreover, such a behavior is seen to be monotonic with particle loadings, with systems of higher loadings exhibiting slower polymer dynamics relative to nanocomposites at lower particle loadings. We note that these trends are broadly consistent with the results presented by Smith and co-workers in refs 54 and 55, which studied PEO matrices near TiO₂ surfaces. Therein, the authors demonstrated that there is densification and dynamical retardation of PEO segments near the surface. We expect similar behavior to manifest near nanoparticle surfaces considered in our present work, which would explain the results of Figure 2. An increase in particle loadings would increase the overall spatial extent of such densified interfacial zones and is consistent with the further retardation in the polymer dynamics seen at higher loadings.

To probe the correlation between the lowering of ionic mobilities (Figure 1) and the polymer segmental relaxation times (Figure 2), in Figure 3 we display a direct comparison of the ionic diffusivities with the inverse relaxation times. While the diffusivities are seen to deviate from the behavior expected

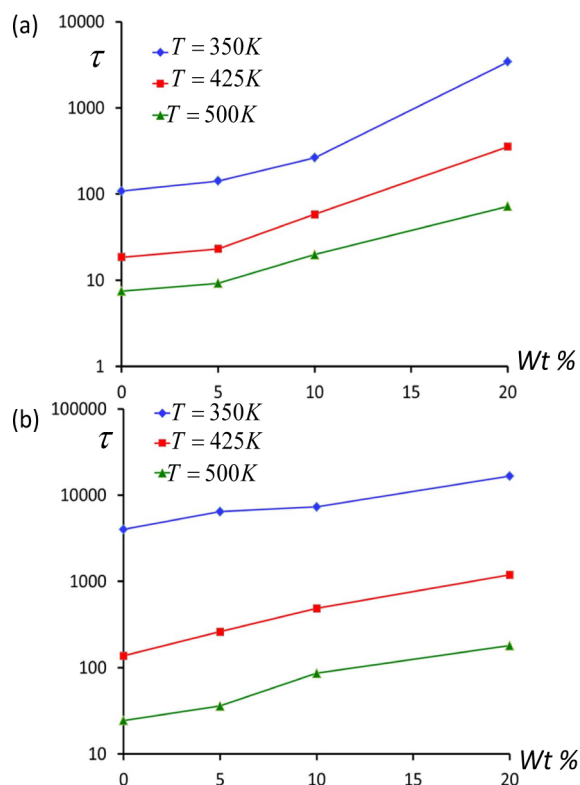


Figure 2. Mean polymer segmental relaxation times τ (in ps) in PEO + TiO₂ nanoparticle matrices as a function of weight percentage of nanoparticles: (a) EO:Li = 15:1 and (b) EO:Li = 8:1. Lines are meant to be a guide to the eye.

from the Stokes–Einstein-like relationship ($D \propto \tau^{-1}$), nevertheless, for both lithium concentrations it is seen that the ionic mobilities are strongly correlated to the modified polymer segmental relaxation times. Such a result suggests that the impact of nanoparticles upon the ionic mobilities arises primarily as a consequence of the influence of the former upon the polymer segmental dynamics.

Ionic motion in polymer electrolytes has been shown to result from a combination of intra- and interchain hops within a complex coordination structure wherein the Li⁺ cations are complexed by multiple segments of the PEO matrix.^{42,56} It has been speculated that the addition of nanoparticles may disrupt the polymer conformations and thereby influence the dynamics of the ions coordinated with the polymer backbone. Motivated by such considerations, we probed the influence of nanoparticles upon the polymer conformational features. Specifically, earlier studies have shown that there is a dominant probability of finding either three or six EO segments within the first coordination shell of Li⁺ ions.⁵⁷ Motivated by such considerations, we examined whether the addition of nanoparticles disturbs the triad and sextet conformers on the PEO chains. For this purpose, the backbone of the PEO molecules was divided into a running series of conformational triads and sextets (–C–O–C–C–O–C– dihedral sequences). The populations of the different conformers were calculated over a short trajectory of approximately 0.4 ns and were used to determine the probability that the dihedral sequence would be a specific conformer. To maintain brevity, below we discuss only the results for the triads, which include *tgt*, *tgg*, *ttt*, *tgg'*, and *ttg* conformers.

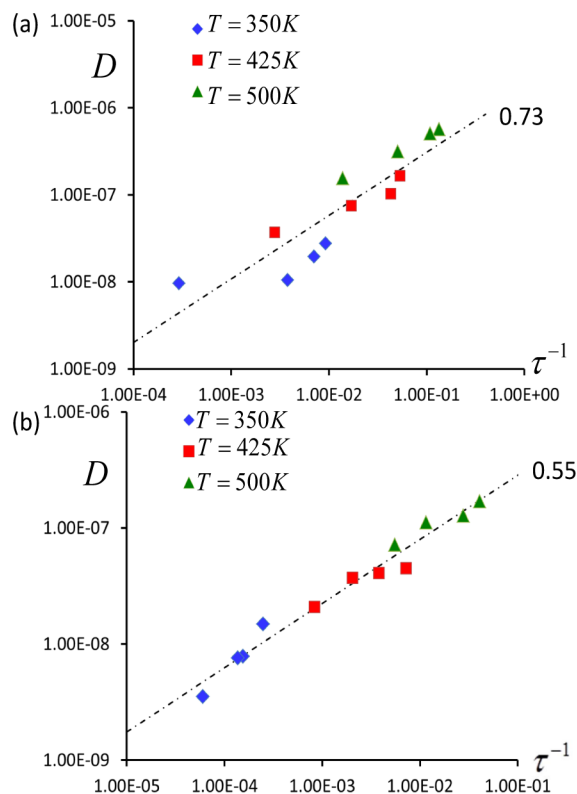


Figure 3. Ionic diffusivities D displayed as a function of inverse of mean polymer segmental relaxation times in PEO + TiO₂ nanoparticle matrices as a function of weight percentage of nanoparticles: (a) EO:Li = 15:1 and (b) EO:Li = 8:1. The different points correspond to the different loadings of the nanoparticles. The dotted line indicates the power law fit to the data, and the numbers correspond to the exponent of such a fit.

In Figure 4a, we display the particle concentration dependence of the populations of the different conformational triads in the PEO chains (the results for other temperatures and 8:1 ion concentrations, which display similar trends, are presented in the Supporting Information). We see that the addition of particles leads to significant changes in the two most dominant conformational triads, viz., the *tgt* and *tgg* conformers. Specifically, with increasing particle concentrations, we observe that the population of *tgt* triads decreases significantly, whereas the conformations of *tgg* increase, albeit to a less significant extent. Moreover, all other conformers *ttt*, *tgg'*, and *ttg* show a slight increase in their populations with particle loading.

Our results of Figure 4a demonstrate that nanoparticles have a strong influence upon the polymer conformations. Since earlier studies have shown that Li⁺ ions exhibit different binding energies to the different conformers,⁵⁷ such conformational perturbations would be expected to modify the dynamics of Li⁺ ions coordinated to the PEO backbone and influence ionic mobilities. However, the strong correlation seen between D and τ in Figure 3 suggests that the polymer segmental dynamics plays a dominant role in influencing the ionic motions. This motivates the question whether there is a relationship underlying the polymer conformational modifications and the resulting polymer segmental mobilities. To address this issue, in Figure 4b we display a comparison of the changes in the probability distribution of *tgt* triads at different temperatures (normalized to their values for unfilled polymer matrices) with the polymer segmental relaxation times. We indeed observe a

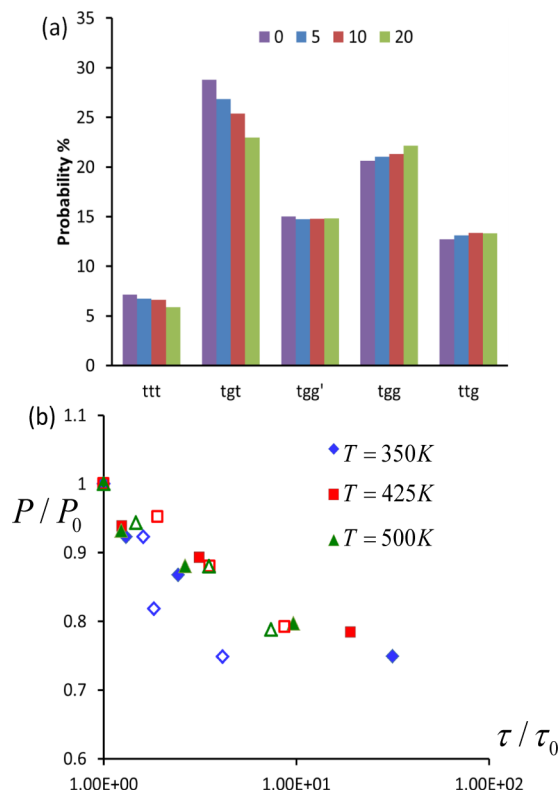


Figure 4. (a) Probability distribution of triad conformers in the PEO backbone as a function of particle concentration ($T = 500$ K) 15:1 EO:Li ratio. (b) Comparison of the probability of *tgt* conformers P (normalized by their values $P - 0$ for unfilled polymers) with the segmental relaxation times τ (normalized by their values τ_0 for unfilled polymers). The points correspond to the different weight fractions of fillers at the different temperatures.

direct correlation between the nanoparticle-induced changes in the polymer conformations and the modifications in polymer segmental relaxation times. Such a relationship serves to rationalize the results presented in Figure 3 and indicates that the correlation between ionic mobilities and polymer dynamics in our system arises in turn from the interdependence of the polymer conformational features and its dynamics.

In summary, we presented results of atomistic MD simulations based on multibody polarizable force fields which showed that the addition of nanoparticles to polymer matrices leads to significant changes in polymer conformations and their dynamics. However, there was observed to be a strong correlation between the particle-induced modifications of the polymer conformations and the polymer segmental dynamics. As a result, ionic diffusivities followed the trends exhibited by polymer segmental dynamics. More generally, our results suggest that ionic mobilities in filled polymer systems strongly correlate with the polymer segmental dynamics when there is a strong interrelationship between polymer conformational features and their dynamics. In future studies, we plan to explore the generality of our results for other polymer–filler combinations.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of the simulation setup, comparison of TEKMC to atomistic simulations, dynamics of PEO segmental relaxations,

and conformational features of PEO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Van Schalkwijk, W. *Nat. Mater.* **2005**, *4*, 366–377.
- (2) Megahed, S.; Scrosati, B. *J. Power Sources* **1994**, *51*, 79–104.
- (3) Scrosati, B. *Nature* **1995**, *373*, 557–558.
- (4) Meyer, W. H. *Adv. Mater.* **1998**, *10*, 439 +.
- (5) Abraham, K. M.; Jiang, Z.; Carroll, B. *Chem. Mater.* **1997**, *9*, 1978–1988.
- (6) Appetecchi, G. B.; Dautzenberg, G.; Scrosati, B. *J. Electrochem. Soc.* **1996**, *143*, 6–12.
- (7) Bruce, P. G.; Scrosati, B.; Tarascon, J. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2930–2946.
- (8) Scrosati, B.; Croce, F.; Panero, S. *J. Power Sources* **2001**, *100*, 93–100.
- (9) Scrosati, B.; Garche, J. *J. Power Sources* **2010**, *195*, 2419–2430.
- (10) Armand, M. *Solid State Ionics* **1983**, *9–10*, 745–754.
- (11) Armand, M. *Solid State Ionics* **1994**, *69*, 309–319.
- (12) Armand, M. *Adv. Mater.* **1990**, *2*, 278–286.
- (13) Ciosek, M.; Sannier, L.; Siekierski, M.; Golodnitsky, D.; Peled, E.; Scrosati, B.; Glowinkowski, S.; Wieczorek, W. *Electrochim. Acta* **2007**, *53*, 1409–1416.
- (14) Gray, F. M.; Maccallum, J. R.; Vincent, C. A.; Giles, J. R. M. *Macromolecules* **1988**, *21*, 392–397.
- (15) Choi, I.; Ahn, H.; Park, M. J. *Macromolecules* **2011**, *44*, 7327–7334.
- (16) Ruzette, A. V. G.; Soo, P. P.; Sadoway, D. R.; Mayes, A. M. J. *Electrochem. Soc.* **2001**, *148*, A537–A543.
- (17) Trapa, P. E.; Won, Y. Y.; Mui, S. C.; Olivetti, E. A.; Huang, B. Y.; Sadoway, D. R.; Mayes, A. M.; Dallek, S. J. *Electrochem. Soc.* **2005**, *152*, A1–A5.
- (18) Christie, A. M.; Lilley, S. J.; Staunton, E.; Andreev, Y. G.; Bruce, P. G. *Nature* **2005**, *433*, 50–53.
- (19) Cho, B. K.; Jain, A.; Gruner, S. M.; Wiesner, U. *Science* **2004**, *305*, 1598–1601.
- (20) Gomez, E. D.; Panday, A.; Feng, E. H.; Chen, V.; Stone, G. M.; Minor, A. M.; Kisielowski, C.; Downing, K. H.; Borodin, O.; Smith, G. D.; Balsara, N. P. *Nano Lett.* **2009**, *9*, 1212–1216.
- (21) Park, M. J.; Balsara, N. P. *Macromolecules* **2010**, *43*, 292–298.
- (22) Tarascon, J. M.; Armand, M. *Nature* **2001**, *414*, 359–367.
- (23) Soo, P. P.; Huang, B. Y.; Jang, Y. I.; Chiang, Y. M.; Sadoway, D. R.; Mayes, A. M. J. *Electrochem. Soc.* **1999**, *146*, 32–37.
- (24) Capuano, F.; Croce, F.; Scrosati, B. *J. Electrochem. Soc.* **1991**, *138*, 1918–1922.
- (25) Kumar, B.; Scanlon, L. G. *J. Power Sources* **1994**, *52*, 261–268.
- (26) Fullerton-Shirey, S. K.; Maranas, J. K. *J. Phys. Chem. C* **2010**, *114*, 9196–9206.

- (27) Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. *Nature* **1998**, *394*, 456–458.
- (28) Sides, C. R.; Croce, F.; Young, V. Y.; Martin, C. R.; Scrosati, B. *Electrochem. Solid State Lett.* **2005**, *8*, A484–A487.
- (29) Croce, F.; Curini, R.; Martinelli, A.; Persi, L.; Ronci, F.; Scrosati, B.; Caminiti, R. *J. Phys. Chem. B* **1999**, *103*, 10632–10638.
- (30) Croce, F.; Sacchetti, S.; Scrosati, B. *J. Power Sources* **2006**, *161*, 560–564.
- (31) Quartarone, E.; Mustarelli, P.; Magistris, A. *Solid State Ionics* **1998**, *110*, 1–14.
- (32) Appetecchi, G. B.; Croce, F.; Dautzenberg, G.; Mastragostino, M.; Ronci, F.; Scrosati, B.; Soavi, F.; Zanelli, A.; Alessandrini, F.; Prosinì, P. P. *J. Electrochem. Soc.* **1998**, *145*, 4126–4132.
- (33) Appetecchi, G. B.; Croce, F.; Mastragostino, M.; Scrosati, B.; Soavi, F.; Zanelli, A. *J. Electrochem. Soc.* **1998**, *145*, 4133–4135.
- (34) Wieczorek, W. *Mater. Sci. Eng. B: Solid State Mater. Adv. Technol.* **1992**, *15*, 108–114.
- (35) Nagasubramanian, G.; Attia, A. I.; Halpert, G.; Peled, E. *Solid State Ionics* **1993**, *67*, 51–56.
- (36) Gang, W.; Roos, J.; Brinkmann, D.; Capuano, F.; CROCE, F.; Scrosati, B. *Solid State Ionics* **1992**, *53*, 1102–1105.
- (37) Johansson, P.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem. B* **2001**, *105*, 9016–9021.
- (38) Wieczorek, W.; Zalewska, A.; Raducha, D.; Florjanczyk, Z.; Stevens, J. R. *J. Phys. Chem. B* **1998**, *102*, 352–360.
- (39) Scrosati, B.; Croce, F.; Persi, L. *J. Electrochem. Soc.* **2000**, *147*, 1718–1721.
- (40) Appetecchi, G. B.; Passerini, S. *Electrochim. Acta* **2000**, *45*, 2139–2145.
- (41) Walls, H. J.; Zhou, J.; Yerian, J. A.; Fedkiw, P. S.; Khan, S. A.; Stowe, M. K.; Baker, G. L. *J. Power Sources* **2000**, *89*, 156–162.
- (42) Borodin, O.; Smith, G. D. *Macromolecules* **2006**, *39*, 1620–1629.
- (43) Borodin, O.; Smith, G. D. *J. Phys. Chem. B* **2006**, *110*, 6293–6299.
- (44) Borodin, O.; Smith, G. D.; Douglas, R. J. *J. Phys. Chem. B* **2003**, *107*, 6824–6837.
- (45) Borodin, O.; Smith, G. D.; Jaffe, R. L. *J. Comput. Chem.* **2001**, *22*, 641–654.
- (46) Maitra, A.; Heuer, A. *J. Phys. Chem. B* **2008**, *112*, 9641–9651.
- (47) Maitra, A.; Heuer, A. *Phys. Rev. Lett.* **2007**, *98*, 227802.
- (48) Maitra, A.; Heuer, A. *Macromol. Chem. Phys.* **2007**, *208*, 2215–2221.
- (49) Hektor, A.; Klintonberg, M. K.; Aabloo, A.; Thomas, J. O. *J. Mater. Chem.* **2003**, *13*, 214–218.
- (50) Kasemagi, H.; Klintonberg, M.; Aabloo, A.; Thomas, J. O. *Solid State Ionics* **2002**, *147*, 367–375.
- (51) Neyertz, S.; Brown, D. *J. Chem. Phys.* **1996**, *104*, 3797–3809.
- (52) Hanson, B.; Pryamitsyn, V.; Ganesan, V. *J. Phys. Chem. B* **2012**, *116*, 95–103.
- (53) Neyertz, S.; Brown, D. *Macromolecules* **2010**, *43*, 9210–9214.
- (54) Borodin, O.; Smith, G. D.; Bandyopadhyaya, R.; Redfern, P.; Curtiss, L. A. *Modell. Simul. Mater. Sci. Eng.* **2004**, *12*, S73–S89.
- (55) Borodin, O.; Smith, G. D.; Bandyopadhyaya, R.; Bytner, E. *Macromolecules* **2003**, *36*, 7873–7883.
- (56) Diddens, D.; Heuer, A.; Borodin, O. *Macromolecules* **2010**, *43*, 2028–2036.
- (57) Borodin, O.; Smith, G. D. *Macromolecules* **1998**, *31*, 8396–8406.