Computational chemistry: design and experimental verification of pre-designed heteropolymer electrolytes for rechargeable lithium batteries

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Abstract

The goal of this work was to establish the efficiency of using computational design to sort through potential solid polymer electrolyte structures, and then verify the computational predictions with a traditional laboratory experimental program. The promise of this approach is demonstrated by the results presented. In this combined computational-experimental program a set of heteropolymer solid polymer electrolytes were first constructed in virtual space and the diffusion of lithium salts predicted as a function of chemical structure, including the salt, and other environmental conditions. These computational predictions were then verified by experimentation. More specifically, some previously untested heteropolymer structures have been designed using modeling, and their lithium ion diffusion rates predicted in comparison to those of known control structures. These new polymers were then synthesized and characterized in the laboratory with the results substantiating the predictions. This has led to an expanded synthesis program, one that is efficient and cost effective.
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1. Introduction

The study of rechargeable battery systems involves a large number of experimental variables. This fact suggests that any technique that works to minimize the number of variables is inherently of great potential value. One such technique involves the use of computational chemistry in the selection and evaluation of potential electrolyte–salt–solvent systems as a function of the chemical structures of the various components. We have been modeling secondary battery systems, more specifically new polymer and salt structures, using molecular dynamic simulations in an effort to correlate the rate of lithium cation and counterion diffusions through a polymer matrix. Our modus operandi has been to screen for superior candidates by structure, and then to synthesize and electrochemically characterize them to verify the simulation results.

Besides the ongoing modeling efforts performed in our laboratory, others have been traveling along similar paths [1–6]. Among other notable recent efforts are those of Kerr [2], Armand et al. [4], Johansson's first principles studies of

ion pairs in polymer electrolytes [5], and Tasaki's molecular dynamics simulations of ionic associations in polymer electrolytes [6]. Our technique has allowed for the selection of new lithium battery electrolyte–salt combinations that possess superior battery performance properties.

2. Computational predictions and experimental verifications thereof

The simulation of lithium chloride in a standard polyethylene oxide (PEO) polymer of varying chain length yielded interesting results as shown in Fig. 1 and Tables 1–3. Lithium chloride was used as a model salt for the sake of calculation speed and simplicity considering the large size of the systems studied. This was done with the recognition of the inherent limitations due to ion aggregation possibilities within the model. Recently, we have extended the simulation studies to include more interesting anions, such as triflate and the perfluorosulfonamide lithium salts. That is, we are finding that more complex salts, such as lithium bis(perfluoroethane) sulfonamide (BETI) are yielding similar qualitative simulation results, which will be reported upon separately. We are also finding a positive

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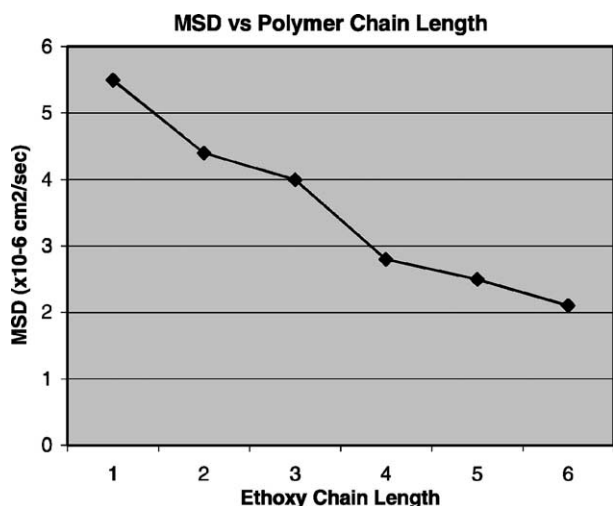*E-mail address:* bdixon@phoenixinnov.com (B.G. Dixon).

Fig. 1. MSD of Li^+ as a function of number of ethylene oxide units in the polymer chain.

Table 1
Predicted ionic diffusion rates of LiCl in polyethers as a function of methylene content[a]

Polymer constitution	D^+ (cm^2/s) ($\times 10^{-6}$)	D^- (cm^2/s) ($\times 10^{-6}$)
$\sim[OCH_2]_n \sim$ (acetal)	2.9	2.9
$\sim[OCH_2CH_2]_n \sim$ (PEO)	2.8	4.0
$\sim[OCH_2CH(CH_3)]_n \sim$ (PPO)	2.8	3.5
$\sim[OCH_2CH_2CH_2CH_2]_n \sim$ (PBO)	2.0	2.0

[a] Li:O ratio of 1:8. Simulations run under NVT protocol.

Table 2
Calculated diffusion coefficients for different polymers and LiCl[a]

Structure	D^+ (cm^2/s) ($\times 10^{-6}$)	D^- (cm^2/s) ($\times 10^{-6}$)
H–[CH$_2$CH$_2$O]$_n$–H **1** (PEO)	2.8	4.0
2 (OCH$_3$ phosphate structure)	8.5	9.0
3 (OPh phosphate structure)	4.5	5.2

[a] Calculations over 100,000 molecular dynamic steps = 100 ps real time.

correlation of ionic diffusion rates with anion structure that parallels that of experimental expectations. This suggests the promise, as yet unexplored by us, of using similar simulation protocols in the design of superior salt conductors.

Table 3
Experimental diffusion coefficients for different polymers and LiCl

Structure	Conductivity (S/cm)
H–[CH$_2$CH$_2$O]$_n$–H **1** (PEO)	7.4×10^{-4} (liquid)
1a	8.0×10^{-7} (solid)
2 (OCH$_3$ phosphate structure)	1.6×10^{-3} (liquid)
3 (OPh phosphate structure)	5.3×10^{-5} (solid)

The modeled prediction of a steady decrease in ionic diffusion with increasing polymer chain length is readily apparent in Fig. 1.

This result fits well with experimental results which show a similar trend [7,8]. It is possible and of interest to extend this set of calculations to longer chain lengths that more closely mimic the real case. This is simply a matter of computational time and hardware speed. The dramatic decrease in computational costs available now make this readily possible, and we are examining this issue. Work by Shi et al. involved the study of PEO molecular weights from 400 to 4×10^6, and showed that above a M_W of 3200 no effectual change was observed [8]. Similarly, Table 1 compares the results of the homologous series of short chain polyethers wherein the methylene spacer is varied. In this case a decrease in ether oxygen content predicts a decrease in ionic diffusion rates, again consistent with intuition and experimentation. That is, the lithium diffusion rate in PBO is significantly lower than the PEO or polyacetal cases.

Of greater interest are simulations of new heteropolymer systems. These were carried out and resulted in the *pre-designed* polyphosphoroxy systems predicted to possess superior lithium diffusion rates compared to the familiar polyethers, such as PEO. We subsequently synthesized examples of these polymers and evaluated their ionic conductivities independently.

Comparative computational and experimental data is given in Tables 2 and 3, respectively.

The last entry (#3) in Table 2 has the P ester OCH$_3$ of model #2 replaced by an electron withdrawing phenoxy ester group. The phenyl substitution resulted in a smaller diffusion constant consistent with more structural rigidity, or fewer degrees of freedom, induced by the aromatic rings. In addition, the electron withdrawing nature of the phenyl rings changes the electron distribution in the chain.

3. Experimental results

The polymers corresponding to entries **1**, **1a**, **2**, and **3** were all synthesized as described and their respective ion diffusion properties determined as described in the following section. The results of the latter are given in Table 3.

From a qualitative standpoint these experimental values of conductivities compare very favorably with the computationally predicted trends. That is, the P-methoxy polymer (entry #2), in this case a liquid, demonstrated to have a significantly better conductivity than the liquid PEG, entry #1. Similarly, the solid poly phenoxy phosphorous compound (#3), was in turn much superior to the solid state PEG (#1a).

4. Molecular simulations and experimental procedures

Calculations were performed under the COMPASS force field. The modeling protocol involved first building a given polymer of 10–20 monomer units, in the absence of the lithium salt, followed by a standard energy minimization of 5000 steps using a combination of Steepest Decent, Conjugate Gradient, and Newton methods in a sequential fashion to yield a reasonable energy based upon a molecular mechanics approach. Similarly, the desired lithium salt was constructed and its energy optimized. At this point the lithium salt of interest was added to the polymer structure at a Li:ether O ratio of 1:8. The salt molecules were distributed more or less evenly along the chain, and located at points in close contact with the polymer chain atoms to represent a high-energy, compact system. The combined polymer–salt was then minimized, again over 5000 steps. This was followed by a molecular dynamics run of between 5000 and 100,000 steps using a microcanonical ensemble, and then another minimization. At each stage the system energy was recorded.

The polymer–salt system was cloned ten times and put into a cell of density = 1 g/cc with boundary conditions to simulate an infinite system. Minimization over 5–10,000 steps followed by a dynamics run as described above over 100,000–500,000 steps, representing 100–500 ps of real time, resulted in a trajectory file for the complete atom system from which the MSD values of lithium cations or the counterion atoms were obtained as separate sets. An important point in the analysis of these various models is that a plot of the logarithms of the displacement versus time values was determined in order to establish the linearity, or constancy, of the ion diffusion as a function of time. In those cases where such linearity was not established, the transport calculations were considered invalid, and were not used.

5. Summary

Our modeling efforts have demonstrated the possibilities of using computational techniques in the design of superior polymer electrolytes for rechargeable battery systems. It is noteworthy also that the dynamic range of calculated values is much narrower than the experimentally determined range, but the reproducibility of both is excellent. Hence small differences in calculated diffusion numbers translate into large differences in real ionic diffusions. Overall, These predictive studies can significantly enhance the rate of return of an associated experimental program. As such it represents a useful and complimentary research tool.

Acknowledgements

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