

Simulation of battery components and interfaces on the atomic scale: examples of what we can learn

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Abstract

In the lithium polymer advanced battery program, the stated target of 10^{-3} (Ω cm) $^{-1}$ for polymer electrolytes at room temperatures is, to our knowledge, not attained by any of the polymer electrolytes in current use in prototypes, without adding plasticizers [F. Gray, Solid Polymer Electrolytes, VCH, New York, 1991, 108–111] or raising the temperature. In the program on which progress is reported here, we are trying to elucidate the mechanism of ion transport in one of the prototype electrolytes, in the expectation that a better understanding will reveal promising directions for the solution of this engineering problem. We are also beginning studies of the polymer–cathode interface. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

We report results of a molecular dynamics study of electrolytes based on polyethylene oxide (PEO) because of the extensive experimental information [1] which is available about it. Previous simulation work on polymer electrolytes based on PEO has been reported, mainly on iodide salts, and with different approaches to the modeling of the amorphous state [2–7]. We have used molecular dynamics techniques to build a model for the polymer [8] and the ions in it and are collaborating with quantum chemist Larry Curtiss, who provides force fields for our models and Marie-Louise Saboungi and David Price of Argonne, who are doing neutron scattering studies. In our method of producing a model of the amorphous polymer, we “polymerize” a model of the monomeric liquid dimethyl ether computationally. We published comparisons between our molecular dynamics model of amorphous PEO and the results of elastic neutron measurements on the neat polymer by our collaborators [9]. We show some examples of more refined versions of this comparison below (Figs. 1

and 2, these figures show weighted radial distribution functions, which measure the local structure of the polymer; see Ref. [9] for detailed definitions). The results depend on some details of the calculations, such as whether we run a simulation at constant pressure or constant volume and on the method of including the hydrogen atoms in the model. Generally, the comparison shows reasonably good agreement of the calculations with the experimental results, though some features in the region of 3–4 Å are persistently different and may indicate that the present model is not getting the trans-gauche ratios quite the same as in the experimental sample. (Note added: Our most recent simulations, at constant pressure and with improved description of hydrogen motion, show better agreement with experiment than that shown in Figs. 1 and 2.)

We studied the structure of isolated lithium and perchlorate ions in the polymer as well [10]. The isolated lithium ion is coordinated by six oxygen atoms from the polymer in the model. This appears to be consistent with recent neutron results.

2. Ion pairing

To use this model to produce insights concerning the nature of the electrolyte which can be useful in battery

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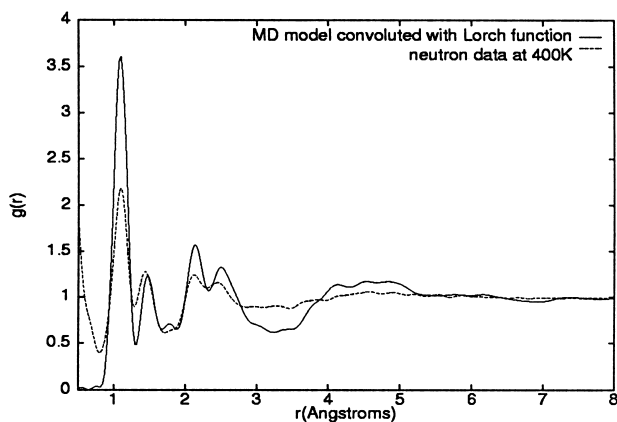


Fig. 1. Weighted radial distribution function calculated from the model for amorphous polyethylene oxide, compared with experimental neutron scattering results (dashes).

electrolyte design, we made a study of ion pairing of lithium perchlorate in PEO [11]. Ion pairing [12–15] is a significant factor limiting ionic conductivity. There is evidence that pairing increases with increasing temperature [16,17] possibly [18,19] because more entropy is available to a pair than to separated ions.

We calculated the potential of mean force between a lithium and perchlorate ion in the system for several temperatures when a pair of ions is at various separation distances in our model. We found evidence at low ionic concentrations for *two* minima in the potential of mean force, one at lithium–chlorine separations of 3.5 Å and about 6.5 Å. We studied the same system with five ion pairs in a system of 216 polymerized monomers and again find two minima at the same separation distances but in this case, there is evidence of entropic effects in the binding free energy of the pairs at 3.5 Å. We have been able to deduce the structure of the paired ion complexes. Fig. 3 shows the distribution of oxygen from the perchlo-

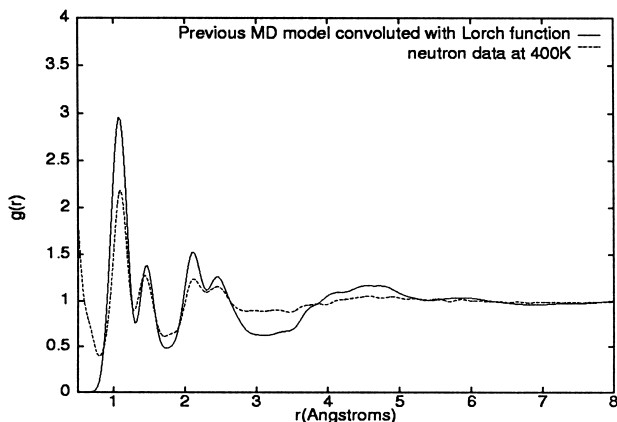


Fig. 2. Weighted radial distribution function calculated from the model with a different algorithm for accounting for the hydrogen positions compared with experimental neutron scattering results.

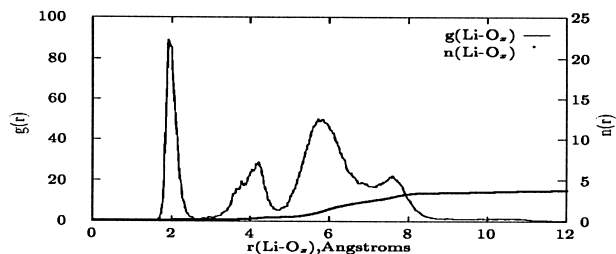


Fig. 3. Distribution of oxygen associated with the perchlorate anion around the lithium cation in the system containing one ion pair in amorphous polyethylene containing 216 monomers at 280 K. r is in angstroms (10^{-8} cm). $n(r)$ is the running coordination number, obtained by integrating the radial distribution function $g(r)$ times an appropriate weighting factor. At large distances, $n(r)$ goes to 4, accounting for all four oxygens in the perchlorate ion. The orientation of the perchlorate in the predicted pair can be deduced from these data as described in Ref. [11]. The peak at 2 Å in $g(r)$ arises from the near pairs. It provides negligible weight in the integral leading to $n(r)$ because the weighting factor is proportional to r^2 .

rate around the lithium in the pairing state at 6.5 Å from the simulation. At higher ionic concentrations of relevance to battery applications and for which neutron data are available, the mean separation of the ions is comparable to the ionic separation in this pairing state. Simulations at these higher concentrations are currently under way. These results on ion pairing, if confirmed by a more detailed analysis of the neutron scattering data, can provide useful guides to design of electrolytes with better conductivity. We will extend these studies to other anions, beginning with triflate.

3. Effects of water

We have made simulations of small amounts of water in our model PEO electrolyte in the presence of lithium ion. PEO is very hydroscopic, so an understanding of how trace amounts of water might behave (possibly even increasing conductivity [23]) could prove useful in battery design. We inserted various numbers of water molecules and one lithium ion in a molecular dynamics sample of amorphous PEO. Three water molecules stably solvate the lithium ion, but four water molecules form a structure in which three water molecules are nearer to the lithium than the fourth one (Fig. 4). Six water molecules appear to solvate the lithium ion in a still more complicated way which is still under investigation. Neutron data is available for the lithium perchlorate water/PEO system and will be analysed to check these results. We are studying the effects of water on the conductivity. These studies may be extended to investigate the behavior of other monomeric additives.

4. Ionic conductivity and future directions

We illustrated the problem of calculating low frequency conductivity [10] by this approach in Ref. [20] where

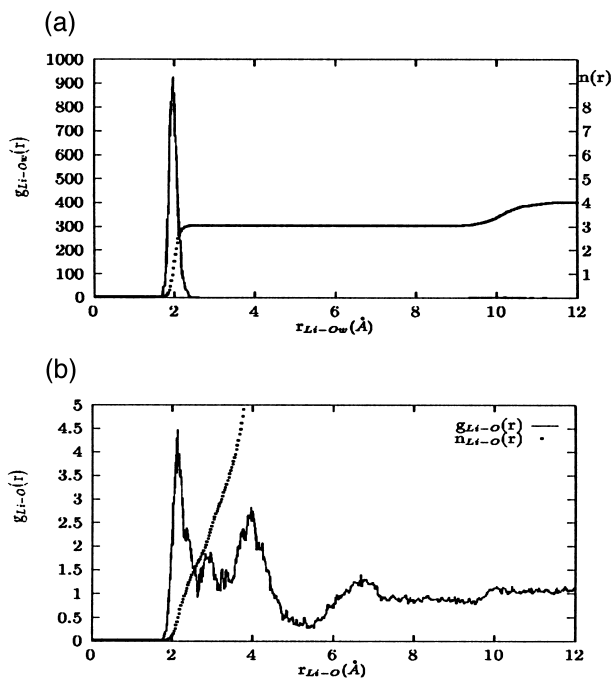


Fig. 4. (a) Distribution of oxygen associated with water around a lithium cation in a model of amorphous polyethylene containing 216 monomers and four water molecules at 280 K. As one can see from the running coordination number $n(r)$, also shown, three water molecules are solvating the lithium ion while the fourth prefers energetically to stay away from the cation. (b) Distribution of oxygen associated with polyethelene oxide around a lithium cation in a model of amorphous polyethylene containing 216 monomers and four water molecules at 280 K. From the running coordination number, plotted as dots, approximately three oxygen centers from the polymer are completing an approximately six-fold solvation of the lithium ion. r is in angstroms (10^{-8} cm).

calculated and measured conductivities [21] are compared (Fig. 5). At comparable frequencies, there is qualitative agreement, but the molecular dynamics model is limited to the frequency range above 10^{10} Hz. To improve this situation, we are developing a method of renormalizing the molecular dynamics model so that it can be used to simulate much longer times and lower frequencies (or larger systems) without sacrificing the accuracy of the long wavelength and low frequency predictions, and without significant increase in computation cost. In Fig. 6, we show preliminary results for the optical conductivity of pure PEO calculated in our model down to frequencies of 10^9 Hz using this technique.

Very recently, there have been several reports that adding very small particles of silica or titanium dioxide to the PEO electrolyte dramatically improves the conductivity. The mechanism by which this occurs is not understood. To provide insight into this question, we plan to use recently developed techniques [22] for modeling oxides in order to study the interface between titanium dioxide and polymer, in the presence of lithium and water. These same

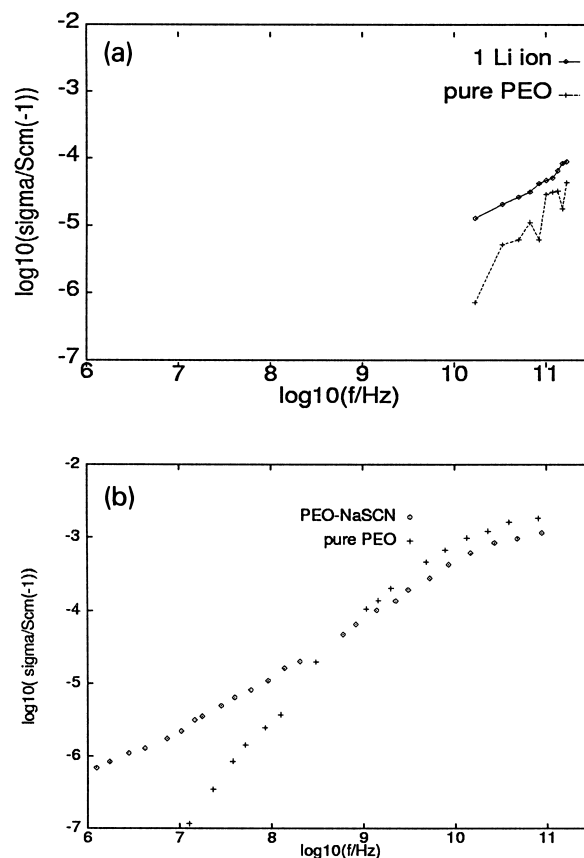


Fig. 5. Comparison of simulated conductivity data (a) with experimental results on PEO with and without salt (b).

methods will be used to study the polymer electrolyte–cathode interface. Classical molecular dynamics is unable to correctly describe the charge screening which occurs as ions enter and move through the electrode.

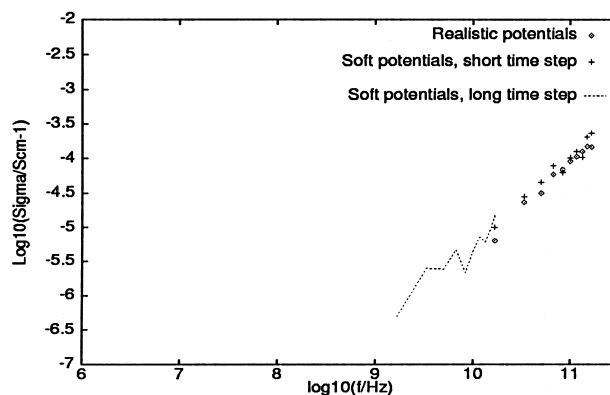


Fig. 6. Calculated optical conductivity for pure PEO in the model using the renormalization technique briefly described in the text. The dashed line shows results obtained with the renormalized model at approximately the same computational cost required for calculating the higher frequency results (symbols) obtained from the same model.

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