

THE CORRELATION EFFECT ON THE CHAIN MOTION CONTRIBUTION TO IONIC TRANSPORT IN POLYMER ELECTROLYTES*

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ABSTRACT

The ionic transport process in polymer electrolytes (such as polyethylene oxide) was simulated numerically on a two dimensional square lattice where charge carriers are accommodated by the lattice sites connected randomly with available bonds to represent the amorphous chain configuration. Following the dynamic bond percolation theory (DBPT), the chain motion contribution to the ionic conduction was incorporated via periodical renewal of the random bond configuration. To check and extend the prediction made by DBPT employing global abrupt bond renewal, spatial correlation of the bond reassignment was introduced to the system by: 1) regional bond renewal and 2) organized bond motion. It is found that the difference between the diffusivities simulated involving regional bond renewal and those of DBPT becomes negligible when the bond renewal rate approaches the carrier hopping rate.

INTRODUCTION

The ionic conducting mechanism for polymer electrolytes such as polyethylene oxide-salt complex ($\text{PEO} + \text{M}^+\text{X}^-$) has been of great interests due to the demand for compact solid state polymer batteries and fuel cells. However, satisfactory microscopic model are still lacking^[1] to describe the formation of, and their transport properties within, polymer electrolytes. This is mainly caused by the fact that the conducting process in these polymer electrolytes is largely promoted by the host polymer chain movement, which has been confirmed by the experimental results that ions are much less diffusive below T_g of polymer electrolytes. It has been suggested that cations, Li^+ or K^+ , are dissociated from the anions and form complex with Lewis bases (oxygen). The ionic diffusion involves the

shipment of the cations from one such site to another and then the anions moving into available holes both via chain segment motion. Such complication disarmed the attempt to employ traditional ion transport theories to explain the complex experimental results.

The only microscopic model available to describe ionic transport assisted by polymer host thus far, has been the dynamic bond percolation theory (DBPT)^[2-8], which utilizes lattice sites to represent bases for ions and randomly assigned bonds connecting the lattice sites to simulate the chain configuration of the host polymer. The motion of the chain segment is achieved by the periodic renewal of random bond configuration, and continuous diffusion of ions is obtained even when the fraction of bonds available is below the percolation threshold of the static lattice. The dc diffusivity (and therefore, the conductivity) is given by ref. [8]:

$$D = n_d \overline{\langle r^2(t) \rangle_s} / t \quad (1)$$

where $n_d = 1/(2d)$ for the Euclidian dimensionality d of the lattice concerned. The mean square displacement $\langle r^2(t) \rangle_s$ can be obtained by static percolation system and the bar indicates the average over t with $\Psi(t)$, a general form of renewal time probability distribution. If $\delta(t - t_r)$ is proposed for Ψ in numerical simulation, the resulting equation becomes $n_d \langle r^2(t_r) \rangle_s / t_r$, similar to that obtained by direct estimation from the mean-square displacement vs. time plot.

To extend the study to the more realistic systems in which bonds may be random walks, instead of global random renewal this report considers first the regional bond reassignment and then the organized bond walking, so that spatial correlation of the polymer chain movement can be included. In our simulation a two dimensional square lattice with spatial disorder of bond distribution is constructed. The host chain motion is simulated first by the regional renewal of the random bond configuration in which the available bonds will be relocated within a zone after each reassignment process. The orientation of the zones are varied to show the effect of the correlation on the diffusion. Then the regional random renewal is modified to become completely correlated bond movement, where the bonds are walking in an organized fashion. The diffusion of ions on these dynamic disordered systems is simulated by setting up proper boundary conditions and the diffusivities are calculated from the slope of the $\langle r^2(t) \rangle$. The DBPT results having abrupt global bond renewal will also be presented to make a comparison. Finally, the singular behavior occurred from the simulation is discussed.

SIMULATION

Following DBPT, the bases accommodating ions are represented by the sites on a 50×50 lattice and polymer chain hosts simulated by the connecting bonds randomly assigned in the beginning. The probability (P_i) of finding an ion at lattice site i is expressed by the master equation(2):

$$dP_i/dt = \sum_j (W_{ji}P_j - W_{ij}P_i) \quad (2)$$

where the sum of $j(=[jx, jy])$ runs over the nearest neighbors of $i(=[ix, iy])$ only. The hopping rate W_{ij} between two neighboring sites (ij) is assigned with either zero (when the bond between site i and j is blocked) or a constant value W , subject to the constrain that the fraction of non-zero W_{ij} 's equals f , the fixed availability. During the numerical simulation, the time step τ (within which all P_i 's are re-evaluated once) was chosen to be $0.2/W$ so that the average hopping time from one site to another is 5τ . The bonds were randomly assigned by a random number generator before the simulation starts with a fixed fraction of 0.2, which is below the static bond percolation threshold ($f_{th}=0.5$) in two dimensions. The diffusion route was set along the X-axis by letting $P=1.0$ on the boundary in X-axis and imposing periodical boundary condition on Y-axis. The mean-square displacement of the hopper was calculated as $\sum P_i X_i^2$ where the sum runs over all sites.

To extend the DBPT results to include spatial correlation of the host chain movement, the global random bond renewal is replaced first by the regional reassignment. A few rows of bonds within a zone extending along X-axis (or Y-axis) are randomly renewed periodically, so that these bonds available for ionic shipment can only be relocated within this zone. Because the fraction of the available bonds is kept constant, the introduced spatial correlation amongst the bonds becomes more evident when a very small zone is considered; the available bonds can only be moved back and forth. Such regional reassignment is repeated successively along Y-axis (or X-axis) to cover the whole lattice, so that all bonds are renewed with a cycle of t_r , the renewal period. This is similar to the situation of having a global renewal with a probability distribution function $\delta(t-t_r)$. The simulation diffusivity D_{sim} is estimated by $n_d \langle X^2(t) \rangle / t$, where t was conveniently chosen to reach tens of renewal cycles.

Secondly, the walking of bonds has been constructed to include not only local^[9], but also long range spatial correlation existing in the polymer chain movement. This "organized bond motion" is realized by sequentially shifting the indices of W_{ij} (where i represents ix, iy) within a row (or a column) when bonds parallel to each other are substituted to simulate the translational motion. This procedure can then be repeated along Y (or X) axis to the rest of rows (columns) to scan through entire lattice, such that all the bonds are reassigned once within a period $t_r (= \lambda^{-1})$ ^[10].

RESULTS AND DISCUSSION

Simulated diffusivities along X-axis were plotted against renewal rate ($\lambda = t_r^{-1}$) in Fig. 1 by curve 2 and 3. The D_{DBPT} , generated by static percolation data and calculated according to $\langle X^2(t_r) \rangle_s / (2t_r)$, was also provided to make a comparison. It is found that for a medium bond renewal rate (e. g. : $\lambda = 0.04/\tau = 0.2/t_h$), the diffusion is faster by the regional renewal of the zones extending along X-axis, parallel to the diffusion route (curve 2). When perpendicular zones are chosen, the resulting diffusion becomes slower (curve 3). This demonstrates the correlation effect raised by the random renewal of the bond configuration within the zone extending along either X-axis or Y-axis. When the bonds available for ionic shipment can only relocate themselves along the diffusion route, their motion contribution toward the ionic transport is larger than that obtained by global reassignment where they can be relocated anywhere. It can be speculated that this enhancement will become more evident when a very small zone is considered. In that case the available bonds will be forced to move back and forth to act as vehicles to transport ions along the desired direction. Since the zones extending along Y-axis can only correlate bonds on the perpendicular direction to the diffusion, the resulting vehicular effect is reduced to be smaller than that of global renewal.

However, the enhancement diminishes when faster reorganization of bonds is engaged (curve 2 and 3 when $\lambda = 0.1/\tau = 0.5/t_h$). This can be explained by the fact that for a renewal rate rapid enough or for typical allowed pathways at any instant short enough the charge carrier will see little physical difference between global host reorganization and the actual

reorganization process occurs beyond its most immediate environment^[8]. When longer renewal time is involved, the spatial correlation effect emerges through the temporal bond renewal sequence; the ion hopping process is impeded by the slow propagation of bond motion along diffusion route (X-axis), while the reassignment is partitioned into perpendicular zones, and vice versa.

The results of organized bond motion were presented by curve 5 and 6 of Fig. 1. Much larger enhancement of diffusion is obtained by the shifting of the available bonds along the X-axis (curve 5), and more reduction of the diffusivity is observed by the bonds walking along Y-axis (curve 6). Contrary

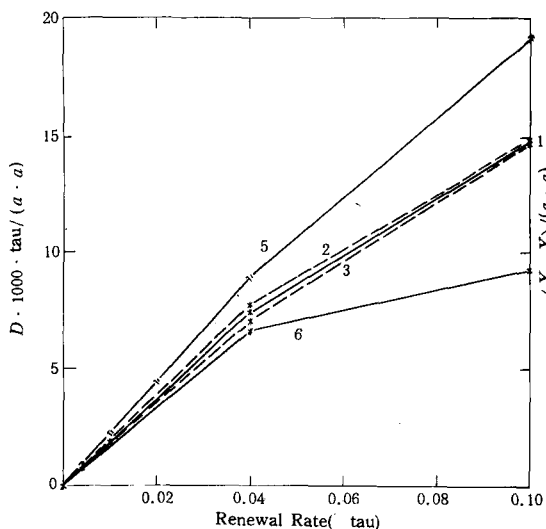


Fig. 1 The diffusivity vs. renewal rate for the dynamic bond percolation model on a two dimensional square lattice (eqn. 2, $f = 0.2$, $W_r = 0.2$). Curve 1; calculated from DBPT with static percolation result; curves 2, 3; D_{sim} 's of regional random bond renewal system with zones parallel and perpendicular to the diffusion route (X-axis), respectively; curves 5, 6; D_{sim} 's of organized bond motion, with bonds walking along X and Y axes, respectively (Errors: $< 1.0\%$)

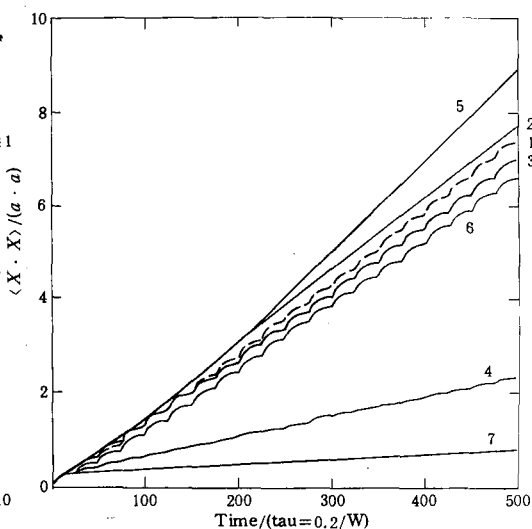


Fig. 2 $\langle X^2(t) \rangle$ vs. t (eqn. 2, $f = 0.2$, $W_r = 0.2$), with constant renewal rate ($\lambda_r = 0.04$). Curve 1; DBPT with abrupt global bond renewal; curves 2 and 3; regional random bond renewal system with zones parallel and perpendicular to the diffusion route, respectively; curves 5, 6; organized bond motion with bonds walking along X and Y axes, respectively; curves 4, 7; the same systems as 3 and 6, respectively, except that the bonds near the origin are immobilized (Errors: $< 1.0\%$)

to the case of regional random bond reassignment, large difference showed at higher renewal rates between bonds moving parallel to the diffusion direction (curve 5) and perpendicular direction (curve 6). This indicates that the long range spatial correlation of bonds caused by the organized motion has drastic effects on the transport properties of the dynamic bond percolation system; when non-correlated bonds are reassigned it is possible to concentrate locally available bonds to furnish occasional passage for carriers, while strongly correlated bond motion will act as powerful conveyors, but only along aligned direction. In real polymer electrolyte systems where spatial correlation of bond is inevitable, such motion is unlikely as revealed by the anisotropic property of the diffusivities simulated here.

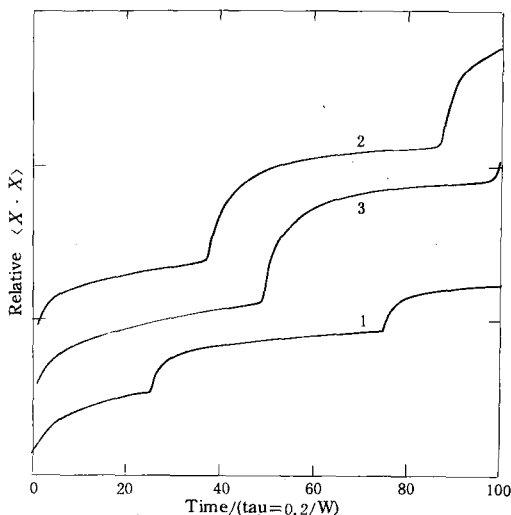
When zones perpendicular to the diffusion route were chosen to execute the regional random bond renewal or organized motion, "stair-cases" were obtained in the $\langle X^2(t) \rangle$ versus time plot (Fig. 2, curve 3, 6). These stair-cases are similar to those found in DBPT with global abrupt bond renewal (Fig. 2, curve 1) which are caused by the periodic acceleration due to the bond rearrangement. However, such were not found when zones were set parallel to the direction of diffusion (curve 2, 5 of Fig. 2) although periodic bond renewal persists. Moreover, these "stair-cases" were found to be largely removed by eliminating the reassignment of bonds near the $X=0$, where the carriers sit before diffusion. In Fig. 2, curve 7 shows the complete removal of the stair-cases for the organized bond motion and curve 4 shows the partial removal in the regional random bond renewal, both by excluding $W_{ix=1, jx=2, iy=iy}$ in the reassignment. These removals were, however, accompanied by sharp decrease of the diffusivities due obviously to the immobilized blocking bonds at $ix=1$.

This singular behavior surrounding the start point of the hopping process was further demonstrated by Fig. 3, where the reassignment of the bonds near origin was relocated to $t = m \cdot t_r + \Delta t$ ($m = \text{integer}$) with $t_r = 50\tau$. The sudden acceleration in the mean-square displacement always coincide with the time instant when bonds near the origin are replaced. It is thus concluded that when perpendicular zones are chosen the bond movement contribution towards the diffusion depends on the spatial location of the bonds.

CONCLUSION

The ionic motion within polymer electrolyte systems was simulated by a two dimensional square lattice with its sites connected randomly with avail-

Fig. 3 $\langle X^2(t) \rangle$ vs. t for organized bond movement (with bonds shifting along Y-axis) showing relocations of the "stair-cases". Curves 1, 2, 3 ($t_r = 50\tau$): location of the first renewal, $\Delta t = 25\tau, 38\tau, 50\tau$, respectively (Errors: $< 2.0\%$)



able bonds to represent the amorphous chain configuration. To extend the prediction made by DBPT employing global abrupt bond renewal, spatial correlation of the bond reassignment was introduced to the system by regional bond renewal within zones and by organized bond motion. The results were compared to that of DBPT engaging abrupt bond renewal. It is found that the diffusivities of regional bond reassignment approach those given by the DBPT when fast renewal is proposed. At slow renewal rate the zones parallel to diffusion route give faster diffusion and vice versa. For the systems involving organized bond motion, the difference becomes larger when reassignment rate increases. It is also found that the singular behavior at the origin where the carriers sit at $t = 0$ is responsible for the periodic acceleration in the growth of the mean-square displacement in certain systems.

Keywords: Ionic diffusion; Chain motion; Two dimensional square lattice; Dynamic bond percolation theory

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