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To cite this article: P L Cheang *et al* 2010 *IOP Conf. Ser.: Mater. Sci. Eng.* **11** 012003

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Modeling of ionic transport in solid polymer electrolytes

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Abstract A Monte Carlo model describing the ionic transport in solid polymer electrolyte is developed. Single cation simulation is carried out using hopping rate to study the transport mechanism of a thermally activated ion in solid polymer electrolyte. In our model, the ion is able to hop along a polymer chain and to jump between different chains, surmounting energy barriers that consist of polymer's activation energy and the externally applied electric field. The model is able to trace the motion of ion across polymer electrolyte. The mean hopping distance is calculated based on the available open bond in the next nearest side. Random numbers are used to determine the hopping distances, free flight times, final energy and direction of the cation after successful hop. Drift velocity and energy of cation are simulated in our work. The model is expected to be able to simulate the lithium-polymer battery in future.

1. Introduction

Polymer-based electrolytes are of growing importance in solid state electrochemistry in view of their applications for high-energy-density batteries used in portable telecommunication devices, computers and even hybrid electric vehicles that are increasing in demand over these two decades [1]. The first suggestion for the use of a poly(ethylene oxide), PEO, based electrolyte in solid-state battery designs was proposed by Armand et al [2] after Wright [3] established ionic conductivity of PEO and inorganic salts complex approaches that of liquid electrolytes. The advantages such as no-leakage of electrolyte, flexible geometry and improved safety hazards besides higher energy density of solid polymer electrolytes (SPE) has since then drawn interest of many researchers. Despite, utility of SPE are still deterred by insufficient cation conductivity in mechanically and chemically stable systems. Microscopic approach for a complete understanding of ion transport mechanisms in SPE is thus essential for the improvement of ionic conductivity in SPE.

Several researches using different approaches have been done on ion transport mechanism in SPE. As the ion is linked to the polymer host, its motion is not free but coupled to polymer dynamic. However, interpreting conduction phenomenon in SPE is not easy as the medium that ions move is statistically disordered and evolving with time. Dynamic bond percolation (DBP) model proposed by Druger et al. [4] is one of the earlier theories that described ion diffusion in one dimensional SPE. A.

Wagner and H. Kliem [5] in 2002 proposed a three-dimensional model for thermally activated ion hopping in a multiwell energy structure by performing dynamic Monte-Carlo (MC) simulations of ionic space charge relaxations. Recently, Maitra et al. [6] characterizes cation dynamics mechanism through analysis of molecular dynamics (MD) simulations on PEO with LiBF_4 under constant density, volume and temperature conditions. In this work, we simulated the velocity and energy of a lithium ion (Li^+) across the SPE using Monte Carlo method.

2. Single Ion Monte Carlo Model

The movement of an ion within SPE involves the breaking of dative bonds to the polymer matrix and the formation of new dative bonds at the new position. Due to the thermal vibrations, ions that receive enough energy would be able to surmount the energy barrier and hop to a nearby vacant lattice site, i.e. the site with open bond and this leads to ion conduction. Therefore, ion transport in polymer electrolytes is a thermally activated hopping process, and low activation energy for bond breaking is essential for a high hopping rate of ions. Free Li^+ , uncomplexed by the anions, are the desirable charge carriers in electrolytic application.

In this work, we propose a transport model of a Li^+ ion moving across polymer electrolytes by simulating its drift velocity and energy at various applied electric fields and at room temperature using single particle Monte Carlo (MC) method. The ion is able to hop along a polymer chain and to jump between different chains (Figure 1), surmounting polymer's activation energy. The motion of Li^+ ion is simulated in the momentum space by choosing the duration of the ion free flights and the hopping events stochastically. The simulation process is illustrated in Figure 2.

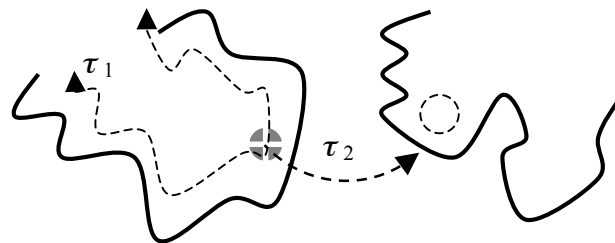


Figure 1. Flight time: τ_1 is the time for ion to hop along a polymer chain, τ_2 is the time for ion to hop to a neighbouring polymer chain.

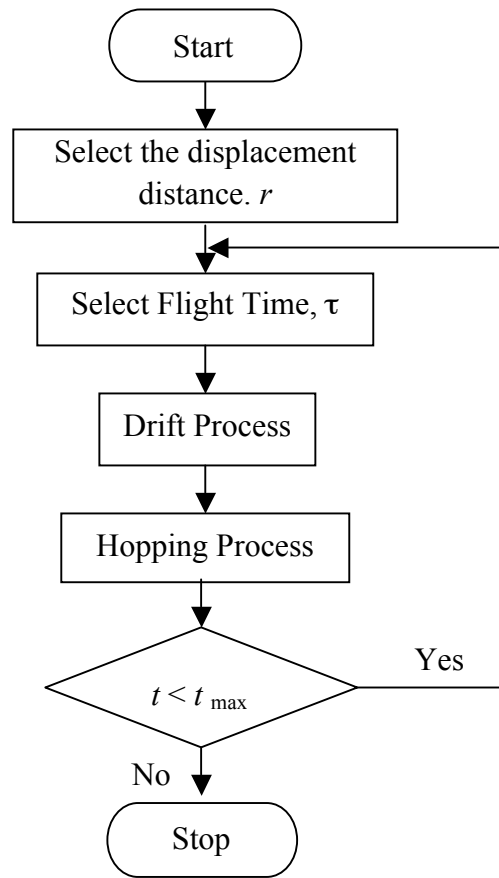


Figure 2. Single Ion Monte Carlo Algorithm.

The displacement of the Li^+ ion is determined as [4]

$$\ell = d \frac{\sqrt{p}}{(1-p)} \quad (1)$$

where d is the lattice space and p is the probability to observe an open bond at the nearest neighbouring site in the polymer electrolyte since the existence of open bond is a basic prerequisite for ionic hopping. The probability for a bond to be open is generated randomly corresponding to the disorder of an amorphous polymeric material.

Besides the availability of open bond, the Li^+ ion must surmount the activation energy of the polymer, which corresponds to the electrostatic binding energy required to break the ion-polymer dative bond and to move the ion away to nearest neighbouring site. Since the ion transport in polymer electrolytes is a thermally activated hopping process, the thermally activated hopping rate is given as

$$s = f_0 \exp(\ell) \exp\left[-\frac{(E_i - E_f)}{kT}\right] \quad (2)$$

where f_o is the attempt to escape frequency and it is set to be 10^{12} Hz, T is the temperature, k is the Boltzmann constant, E_i and E_f are the energies before and after hopping respectively.

The simulation is started by selecting an arbitrary wave vector as the initial condition of the ion, and is allowed to proceed until many flights and hopping events have occurred. The duration of flight time in each iteration is determined by,

$$\tau = -\frac{\ln r}{s_o} \quad (3)$$

where r is a random number and s_o is the initial hopping rate. Only the x -component of the electric field is assumed non-zero. The flight time determined is used to calculate the velocity and energy of ion during drift process. The total flight time must be long enough so that the initial condition has little influence on the final results. Wave vector updated during drift process is transferred to the hopping process. After the free flight, the ion with energy greater than the polymer activation energy will hop. In the hopping mechanism, we have to identify first the hopping mechanism by which the ion hop and then determine the ion state after hopping. The simulation process repeatedly evaluates the drift motion under a constant electric field followed by hopping and so on until the maximum flight time achieved.

3. Results and Discussion

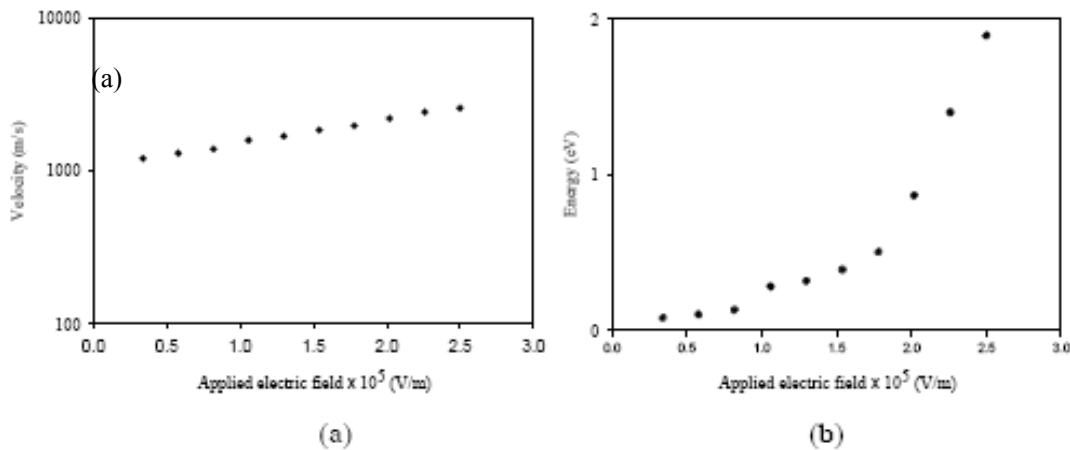


Figure 3. The (a) velocity and (b) energy of ion versus electric field.

The conductivity of SPE has been extensively studied by using various theoretical models to describe the motion of ion. The conductivity of SPE generally depends on the concentration of ions and its surrounding temperature. The velocity of ion and its energy which are required to calculate the conductivity of SPE at room temperature are simulated in our MC model by incorporating hopping process. The velocity and energy of ion at various electric fields are shown in Figure 3. As shown in Figure 3 (a), the velocity of ion increases as the electric field increases. Since the ion is moving in the

direction of electric field, the increase electric field enhances its motion. The ion is excited and becomes more energetic. The energized ions are capable to jump into nearest site especially at higher electric field. A more energized ion is also possible to jump to the nearest neighboring chain as shown in Figure 1. The increase electric field increases the energy of the ion is shown in Figure 3(b).

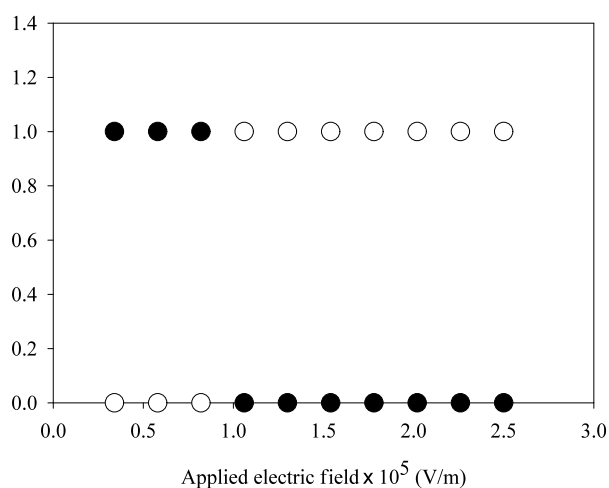


Figure 4. The occupation of ion in chain 1 (closed-symbol) and chain 2 (open-symbol) at various electric fields

When the electric field is lower than 100 kV/m, as shown in Figure 4, the ion is hopping along the first polymer chain as the energy of ion is still insufficient for it to hop across the chains. When the electric field exceeds 100 kV/m, the ion gains enough energy and able to hop to next nearest chain. For electrochemical application, the activation energy for polymer should be less than 0.3 eV [7]. Refer to Figure 1(b), the energy of ion when it first appears at neighboring chain is 0.28 eV. Thus, the polymer in our model has activation energy less than 0.28 eV. Our model is therefore able to model the electrical properties of polymer battery.

4. Conclusions

A Monte Carlo model based on stochastic processes was applied to simulate the velocity and energy of an ion in polymer electrolytes. Both the velocity and energy of the ion increase with increasing electric field. Thus, increase electric field helps to enhance the movement of ion within SPE. Also, the activation energy of polymer in the model is found to be less than 0.28 eV and hence suitable to be used to describe the ion transport in SPE for Li ion polymer battery.

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