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Molecular dynamics simulation of lithium ion mobility in a PEO surface

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Abstract

A model for a poly(ethylene oxide) (PEO) host polymer surface, which was developed earlier, is exploited to probe the ionic distribution for Li^+ and Cl^- ions in the PEO surface for an effective composition $\text{LiCl} \cdot (\text{PEO})_{213}$ at 400 K. The local structural situation around the Li^+ ions was analyzed specifically. Two general situations are observed: Li^+ ions lying deeper into the bulk tend to be associated with one Cl^- and two oxygens; nearer the surface, they coordinate five ether oxygens belonging to the same PEO chain. The ratio between the two cases ($\text{Cl}^- + 2\text{O}:5\text{O}$) moves smoothly from ca. 30:70 in the bulk to ca. 45:55 in the surface region. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molecular dynamics simulation; Ion mobility; PEO surface

1. Introduction

Poly(ethylene oxide) (PEO)-based polymers have attracted considerable attention as potential polymer electrolytes in modern electrochemical devices, especially in high energy-density lithium-ion polymer batteries [1,2]. The physical properties of solid polymer electrolytes directly reflect the structure of the host polymer and its interaction with incorporated salt ions. In the absence of definitive experimental observations, molecular dynamics (MD) simulation is a powerful tool to provide structural insights at the atomic level into the processes involved [3]. Mechanisms relating to ionic transport in a polymer surface have a special relevance to the situation in a Li-ion polymer battery, and yet are very poorly understood.

Of prime interest in this context is the electrochemically active polymer–electrode interface, especially since much of what is stated in this connection has a distinctly weak experimental basis. Potentials developed earlier to model crystalline and amorphous PEO bulk situations [4,5] were later used for the simulation of a ‘crystalline’ PEO surface [6]. This model is used here to describe the PEO host surface for the introduction of a low concentration of Li^+ and Cl^- ions. An ether oxygen:Li ratio of ca. 200:1 is used to probe the ion–polymer interaction.

2. The calculations

The PEO surface model used here is almost identical with that used in our earlier PEO simulations [4,5]. It is based upon the unit cell of crystalline PEO: monoclinic, $\text{P}2_1/\text{a}$, containing two right- and two left-handed helical chains running in the z -direc-

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tion. A $2 \times 2 \times 8$ unit cell simulation box has been used with dimensions: $a = 16.10 \text{ \AA}$, $b = 26.08 \text{ \AA}$, $c = 155.84 \text{ \AA}$, $\beta = 125.4^\circ$ [4,5]. A surface is realized through the creation of a highly asymmetric simulation box comprising 122 \AA -thick 'crystalline' PEO sheets extending in the z -direction, interleaved by a 200 \AA gap (Fig. 1). The first 16 PEO units of each chain, $-(\text{CH}_2-\text{CH}_2-\text{O})_n-$, are tethered to one side of the PEO slab, thus providing a physically realistic structure for the Ewald summation of the local potential experienced by the untethered region on the opposite side of the slab. Three Li^+ and three Cl^- ions were introduced randomly in different ways into the ca. 75 \AA -thick untethered region (Fig. 2). The potential model used and the initial atomic coordi-

nates for the polymer were taken from MD simulations of the crystalline [4] and amorphous [5] PEO phases. A Universal Force Field (UFF) approach was used to calculate the potential parameters for the Li^+ and Cl^- ions [7–9]. The parameters used in the Buckingham and electrostatic terms of the potential are given in Table 1. An Ewald summation method [10] was used in calculating the total potential, with a separation parameter value (a) of 0.34 \AA^{-1} and reciprocal-space cut-offs of $K_a = 6$, $K_b = 7$ and $K_c = 25$. All calculations were made on the IBM Power SP computer at the Parallel Computer Centre (PDC) of the Royal Institute of Technology (KTH), Stockholm, using a local modification of the MD program DL-POLY 2.1 [11]. All simulation were performed

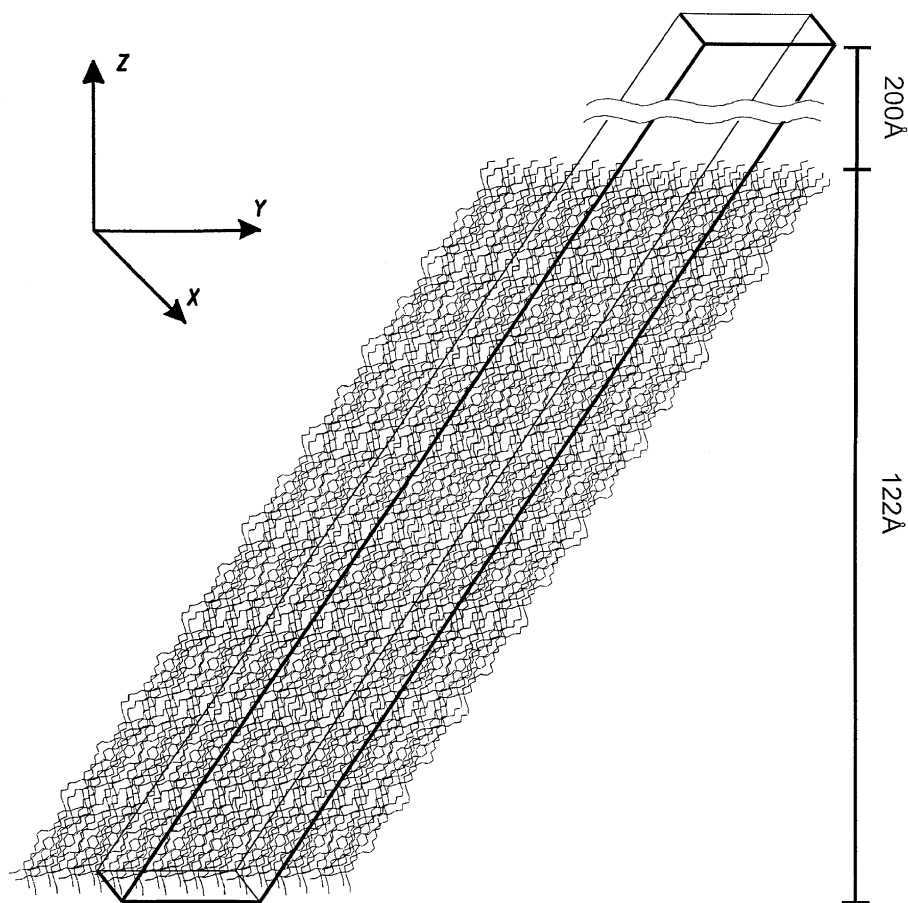


Fig. 1. The MD surface model used in the simulation; the simulation box comprises a 122 \AA -thick 'crystalline' PEO sheet stacking in the z -direction, interleaved by a 200 \AA gap. The first 16 PEO units of each chain are tethered to one side of the PEO slab (see text).

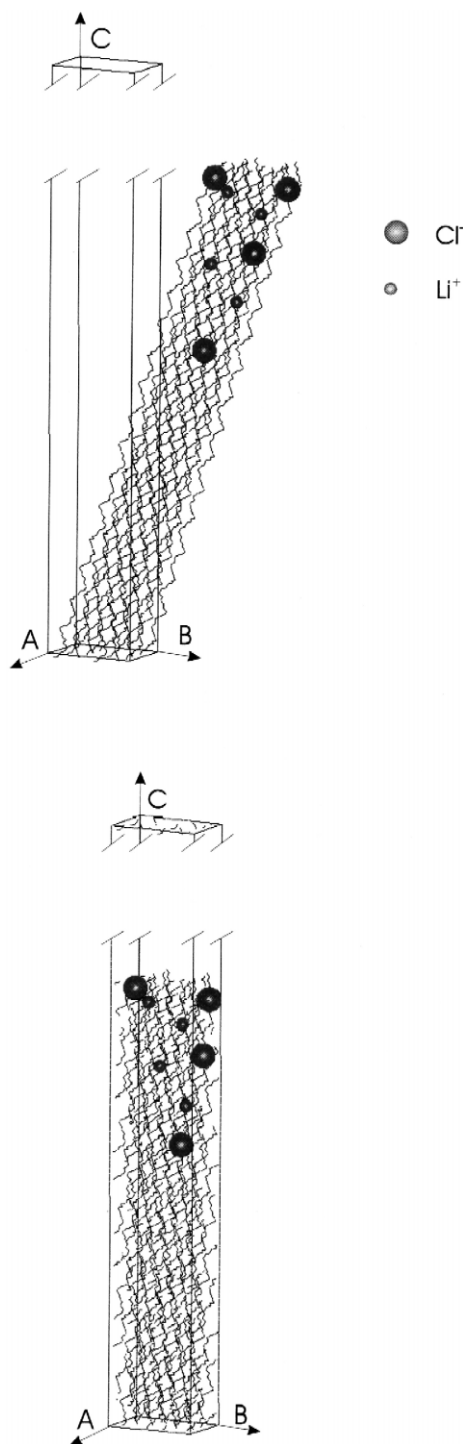


Fig. 2. The start positions for three Li^+ and three Cl^- ions introduced randomly in into the ca. 75 Å-thick untethered region of PEO in the simulation box.

Table 1

The parameters used in the simulation to describe the potential of the form $V(r) = A \exp(-r/B) - C/r^6$ involving the Li^+ and Cl^- ions; other potentials are described in Refs. [4,5]

		A	B	C
Li	Li	4068.90	0.20	10.84
Li	Cl	38820.00	0.23	123.83
Li	C	11272.00	0.25	83.73
Li	O	14696.00	0.23	45.41
Li	H	5398.00	0.22	23.48

at a nominal temperature of 400 K and at a pressure of 1 bar. This temperature had proved optimal in following surface phenomena in our previous surface modelling work, even though its value may have no precise physical relevance [6]. For each set of start coordinates for the ions, the system was allowed to relax for an initial 200 ps using an NVT ensemble simulation. An NpT Nose–Hoover barostat, with relaxation times of 0.1 and 1 ps, was then used in the final 3 ns of simulation. Data were stored for the last 2 ns of this period at 1 ps intervals, for subsequent analysis.

3. Results and discussion

The structural and dynamical information is extracted from the recorded sequence of atomic position and velocity coordinates obtained through the MD procedure described above. In maintaining an

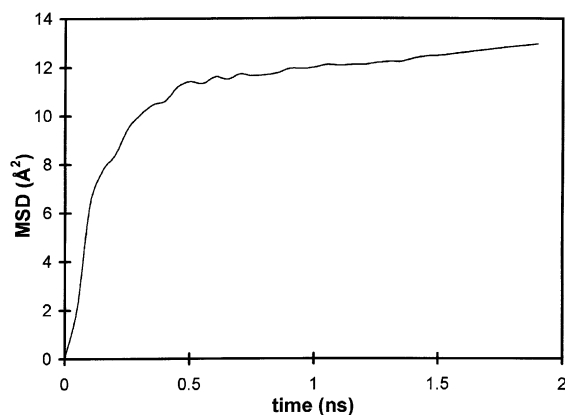


Fig. 3. The averaged mean-square displacement (MSD) for Li^+ ions plotted against simulation time.

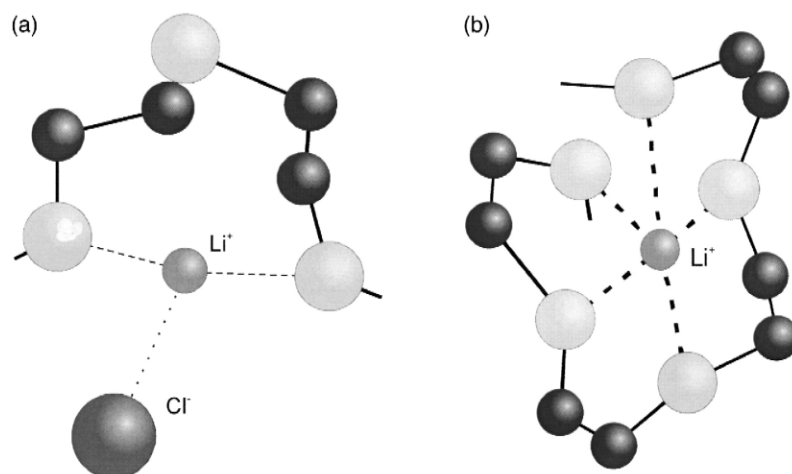


Fig. 4. Local structures showing two typical situations for Li^+ ions: either (a) with one Cl^- and two ether oxygen neighbours (' $\text{Cl}^- + 2\text{O}$ '), or (b) five ether oxygen neighbours (' 5O ').

isotropic pressure tensor in the NpT ensemble, the MD cell expands by roughly 8% during the NpT simulation. Crude 3D diffusion coefficients (averaged over 200–500 ps) were calculated to a value of $1.0 \times 10^{-7} \text{ m}^2/\text{s}$ for Li^+ and $1.0 \times 10^{-9} \text{ m}^2/\text{s}$ for Cl^- ions. It must be stated, however, that despite relatively long simulation times, these 3D diffusion coefficients cannot be determined to any degree of accuracy. Much longer simulation times are needed. This is well illustrated by the behaviour of the averaged mean-square displacement for Li^+ ions plotted against time in Fig. 3.

It is of interest to follow the local structures involving individual Li^+ ions. Two situations are

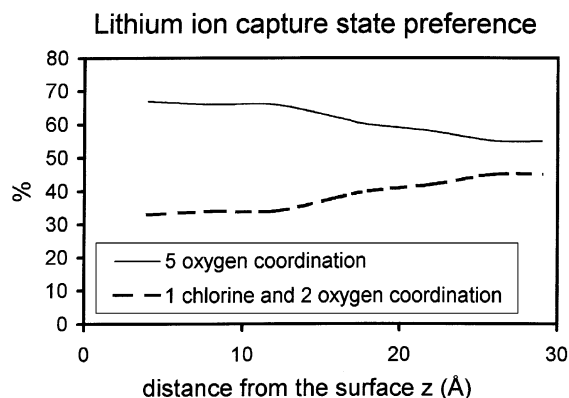


Fig. 5. The incidence of the two cases: ' $\text{Cl}^- + 2\text{O}$ ' (a) and ' 5O ' (b) exemplified in Fig. 4.

observed: Li^+ ions are associated either with one Cl^- and two oxygens (Fig. 4a), or with five oxygens (Fig. 4b). In the ' $\text{Cl}^- + 2\text{O}$ ' case, a symmetrical planar configuration was found with an $\text{O}-\text{Li}^+-\text{O}$ angle of ca. 70° and with the Cl^- ion lying on the bisectrix of this angle. Interchanges between these two situations ($\text{Cl}^- + 2\text{O} \leftrightarrow 5\text{O}$) are also analyzed. No systematic trends can be discerned in these processes, however, although a plot of the incidence of the two cases reveals that the ' $\text{Cl}^- + 2\text{O}$ ' mode predominates deeper into the bulk (Fig. 5), yet still far enough away from the pinned region for this not to be an artefact of the pinning process. The ratio between the two cases ($\text{Cl}^- + 2\text{O}:5\text{O}$) moves smoothly from ca. 45:55 in the bulk to ca. 70:30 in the surface region at 400 K. Unlike in earlier simulations, a very occasional case occurred of a Li^+ ion being coordinated to five O's belonging to two *different* PEO chains; this situation was only encountered deeper into the bulk (at depths greater than ca. 30 Å), where the ' $\text{Cl}^- + 2\text{O}$ ' situation normally dominated. The local structures in such cases correspond closely to the crystalline structure, however.

4. Conclusions

We have shown that our earlier derived crystalline bulk model can be adapted appropriately to provide a

simplistic model for a PEO surface host into which Li–salt ions can be introduced. The behaviour of a low concentration of Li^+ and Cl^- ions has been investigated. A smooth depth-dependent transition between two local structural situations could be extracted from the simulations, with Li^+ ions associated either with one Cl^- and two oxygens deeper into the bulk, or with five oxygen in the surface layer, where the ether oxygens atoms in each case invariably belong to the *same* PEO chain.

Acknowledgements

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