Simulation of ion transport through poly(ethylene oxide) loaded with lithium perchlorate[*]

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A hierarchical approach is used to simulate lithium ion motion through poly(ethylene oxide) loaded with lithium perchlorate, alone and with a tungsten oxide (WO_3) interface to model an electrochromic smart window assembly. The structure of the polymer is simulated using commercial software. Relaxation of the polymer is allowed on a lattice on which the lithium ions move as a lattice gas. Polarization and van der Waals energy changes are calculated for an added lithium ion at each lattice point. The structure and energy are also calculated in the presence of the WO_3 interface. Ion transport is simulated in a kinetic Monte Carlo method, with and without an electric field. During runs at 300 K without the WO_3 interface, with a field the lithium ions move 35 Å along it and 3–7 Å across it but without a field they move 2–5 Å; these distances vary with temperature as expected for activated hopping. Ions explore their immediate neighbourhood, occasionally jumping to an adjacent neighbourhood along, across or sometimes against the field, thus circumventing regions where transport is hindered. With the WO_3, the lithium ions tend to accumulate at the interface, producing a repulsive potential that reduces ion movement.

Key words: *ion transport simulation; lithium perchlorate; poly(ethylene oxide); tungsten oxide; electrochromism*

1. Introduction

Windows are important contributors to the comfort of the occupants of a building but also to the cost of operating the building. Windows admit natural light, which is usually found preferable to artificial light and saves on cost. However, natural light

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may cause glare, and may add significantly to the thermal load on a building, depending on the latitude, climate and season, so increasing the cost of air conditioning. In order to admit maximum light, windows need to be large and thin, but they then provide poor thermal insulation that adds to the cost of heating or cooling to maintain a comfortable temperature inside the building when the temperature outside is much lower or higher.

Advanced glazing improves the balance between cost and comfort [1]. Modern glass can be made with reduced thermal conductivity and coated for high infrared reflectivity. Sealed-unit evacuated double glazing using such glass reduces heat transfer. Significant improvement then requires 'smart windows', with control of the optical behaviour of the glazing which can be achieved by adding an electrochromic thin film confined between transparent electrodes [2]. Changing the electric potential across the electrodes changes the optical transmission through the glazing. For this purpose, the electrochromic material needs to have a large difference in absorption between the colourless and coloured states. It needs to change colour quickly, remain coloured stably, and remain effective over many colouration cycles.

A standard electrochromic material such as tungsten oxide (WO_3) changes colour because the electronic state of the tungsten changes [3]. When this happens, electrical neutrality requires the reduction of the tungsten oxidation state to be balanced by an influx of cations M^+ according to

$$WO_3 \,(\text{colourless}) + y e^- + y M^+ \rightleftharpoons M_y WO_3 \,(\text{blue}) \tag{1}$$

Commonly lithium ions are the cations, supplied by a polymer electrolyte acting as an ion-storage layer with a suitable counter-anion. The transport of lithium ions through the polymer electrolyte material to the interface with the electrochromic material is then an important factor in the performance of the electrochromic component.

Since it was found that poly(ethylene oxide) (PEO) containing alkali metal salts displayed high ionic conductivity [4], solid polymer electrolytes have been extensively studied. Usually made by dissolving a 1:1 electrolyte in a host polymer, they can be regarded as ionic solutions in a basically immobile solvent. If the lattice energy of the salt is low enough and solvating power of the polymeric solvent is high enough (e.g., via complexation of the alkali cation by oxygen lone pairs on the ether subunits) then a thermodynamically well-defined homogeneous and stable phase can be produced. Such materials have potential applications that include all-polymer high energy batteries, artificial muscles, smart windows and biosensors.

Although classified as solids, these materials can have charge transport mechanisms that are more like those in liquids, and very different from those in inorganic crystals because the polymer host is not rigid, so that chain motion can make an essential contribution to the ion transport. Ion-conducting polymers can therefore be thought of as electrolytes that are intermediate between solids (defect crystals) and liquids (solutions and melts) [5]. Studies of processes in such systems must therefore look at the interplay between the observed properties and the polymer structure. For

example, it was originally thought that the ions moved primarily through the crystalline regions of these polymers [6] but later it became clear that the ion transport was primarily through the amorphous regions [7], where dynamic pathways for Li^+ transport are created [8]. Even crystalline polymers exhibit extensive disorder, and in a non-crystalline phase there is quite well defined short-range order and primary chemical structure but a typical radial distribution becomes featureless after a few repeat distances. Moreover, if the polymer is above its glass temperature, even the average order evolves as the structure relaxes. Hence one need to consider transport of charge in a host medium that undergoes microscopic structural reorganization as the carriers move [9].

Such consideration is complicated by the interaction between the polymer and the mobile lithium ions. The phase is stabilized by the attraction between the lithium ions and the coordinating oxygen atoms, but local segment motion can facilitate ion motion via 'Red Sea events': the polymer moves, opening a void adjacent to an ion, which quickly moves into the void, leaving an equivalent void that closes by further polymer movement [10]. Because amorphous regions of the polymer contain more easily redistributed free volume than crystalline regions, conductivity should be much higher in amorphous regions, and so increasing chain mobility generally increases conductivity [8, 11]. However, coordination with Li^+ tends to reduce the motion of the associated polymer segment, leading to two segment relaxation processes, a slower one for such coordinating segments and a faster one for other segments, as observed [12] in the system poly(vinyl methyl ether)–$LiClO_4$. The polymer may also be more actively involved in ion transport if a segment moves carrying with it a coordinated ion, which then transfers to coordinate to another segment or chain, a process we describe as 'octopus football'.

The work reported here forms a part of a project to develop electrochromic evacuated advanced glazing. As explained above, this offers control of solar radiation and high thermal insulation, thereby improving lighting levels and thermal comfort while reducing space heating and cooling loads, electricity demand and carbon dioxide emissions. Our work simulates lithium ion transport through a PEO electrolyte loaded with lithium perchlorate, $LiClO_4$. This material exhibits multiple phases: a salt-rich crystalline phase with conductivity appreciable only above 65 °C [13], a pure PEO spherulite crystalline phase, and an amorphous phase with dissolved salt, where the ion conduction primarily takes place [7, 14]. We also study the effect of an interface between the polymer electrolyte and tungsten oxide. For present purposes, the key physical process is transport of a lithium ion to the tungsten oxide interface. Once there, it can be transported into the bulk and participate in the electrochromic colour change, a process being studied separately as another part of this project [15]. However, the tungsten oxide does affect transport of the lithium ion by changing the energetics in the vicinity of the interface.

Our approach is to model all aspects of the system theoretically: the structure, the energetics of the ions in this structure, and the motion of the ions in this energy land-

scape. We adopt a hierarchical approach whereby more phenomenological methods are validated by comparison with methods that are closer to first principles. This makes the treatment relatively economical in terms of computer time, and makes it simple enough to be practicable for screening new candidate electrolyte systems. Even so, we need complicated potentials to model the interactions in our system, and a particular issue is the hierarchy of relaxation processes, from local processes such as changes in bond angle to the movements of whole segments already alluded to. Molecular dynamics (MD) is a preferred method for providing an atomic description of dynamical behaviour, and has been applied to Li^+ in PEO [16], but even with very long computer simulation runs, MD models time periods much shorter than realistic ion transit times. We therefore use a lattice polymer model [17], in which the atoms of the polymer are allowed to move, but only on a relatively coarse grid of points, with the ions moving as a lattice gas on the same grid. The time evolution of the system is then determined by the Monte Carlo (MC) method. For a single atom at site i with energy E_i moving to a neighbouring site j the dwell time t_{ij} is calculated as

$$t_{ij} = -\ln R \, \exp\left(\frac{E_j - E_i}{kT} \right) \tag{2}$$

where R is a random number uniformly distributed between 0 and 1. The move with lowest dwell time for the atom is carried out, this dwell time is subtracted from all other dwell times, and the energy differences are recalculated.

This paper is organized as follows. We first describe the calculations of the background structure and energetics, which have been presented in detail elsewhere [18]. We then explain how we model the interface between the polymer electrolyte and the tungsten oxide electrochromic material. We simulate the lithium ion transport in this energy landscape and finally draw conclusions from the work.

2. Polymer electrolyte structure

We simulate background polymer electrolyte structures using the Cerius[2] software package from Accelrys Inc. We have previously shown that for calculating dielectric response [19] and polarization energies [20] in poly(ethylene) [20], this package gives structures equivalent to those given by advanced MD simulations. Here the PEO simulation cell comprised five polymer chains each of 200 ethylene oxide segments, plus 50 lithium ions and 50 perchlorate ions at the density of 1.125 g/cm^{3}. This corresponds to loadings in practical electrolyte systems. The structures prepared using the software are relaxed by energy minimization (4000 iterations with the Cerius[2] Minimizer) and then an MD run (4 ps with a time step 1 fs at constant *NVT* for $T = 300$ K).

The simulation requires a suitable energy function to describe the conformational energy of the polymer, its interactions with the ions, and the interactions among the ions. For the polymer, we have explored the potentials due to Smith et al. [21] and to

Lin et al. [22] but eventually use a slightly extended form of the universal force field (UFF) [23] because it provides a potential that can also be used to model tungsten oxide. The UFF comprises a Morse potential bond stretch term, cosine bond bend and torsional terms, and a Lennard–Jones nonbonding term. In order to keep the tetrahedral geometry of the perchlorate ions with the Cl–O bond length about 1.45 Å, consistent with a study [24] of the ion pairing in LiClO$_4$, we modify the valence bond radius r_I and angle q^0 in the potential for Cl from the published values (the second and third columns of Table I in Ref. [23]) to 0.792 Å and 109.47° respectively; the obvious alternative of imposing a rigid geometry is not practicable in the approach we adopt. Finally, because our calculation of the motion of a mobile lithium ion depends in an essential way on its energy of which its electrostatic energy is an important component, we supplement the UFF parameters with the partial charges on the atoms shown in Table 1, taken from a previous study of the PEO–LiClO$_4$ system [25]. To speed up the calculations, we impose a cut-off radius of 6 Å beyond which all long-range potential terms are neglected. However, if during the calculation of the energy differences $E_j - E_i$ an atom initially within this cut-off radius moves outside it, then we retain the atom in the calculation so as to minimize any discontinuity.

Table 1. Atomic partial charges used with the UFF

Atom	Li	Cl	O in ClO$_4$	O in PEO	C	H	W	O in WO$_3$
Partial charge	1	1.0092	–0.5023	–0.326	0.163	0	2.6	–0.9

The structures show a variety of environments for lithium ions, from an isolated ion surrounded by polymer to small clusters of ions and perchlorate counter-ions in a polymer matrix. The calculated static structure factors are in satisfactory agreement with those obtained from full molecular dynamics simulations and in reasonable agreement with these from experiments on perdeuterated PEO. A lithium ion is typically coordinated to 3–6 atoms on a single PEO chain, close to the cation coordination in crown ethers [26].

3. Energetics of a mobile lithium ion

A key component of the energetics of the ions in the material is their electrostatic energy. This comprises two components. One is the Coulomb energy of interaction between the ion and the other ions and between the ion and the permanent charge distributions of the polymer molecules modelled by the atomic partial charges. The other is the polarization energy between the ion and the changes it induces in the charge distributions of the surrounding molecules. We have described the calculation of the electrostatic energy in detail elsewhere [18]. For present purposes, we require the change in the electrostatic energy on adding a lithium ion, which is in effect the chemical potential.

For the purposes of calculating the ion transport, we superimpose a 100×100×100 cubic lattice on the simulation cell, corresponding to a lattice spacing of 0.42 Å. We then calculate the energy of the added lithium ion at every position on this lattice, subject only to the condition that points on the lattice are forbidden if they lie too close to another atom. This amounts to imposing a hard-core repulsive potential. During the simulation the atoms of the polymer are allowed to move on the same lattice to adjust to the ion movement.

4. Effect of interface with WO$_3$

The tungsten oxide affects the energy of an ion in its vicinity and thereby affects the transport of ions to the interface, through which they must travel as a part of the electrochromic colour change process. There are again two contributions to the energetic difference near the interface. One is the change in the force field near the interface. In order to model this, we use the UFF, because it is capable of describing any element, although we do have to derive some parameters. We add terms to the UFF for W and for O in WO$_3$, including the partial charges as shown in Table 1. These are taken from Mulliken analysis of electronic structure calculations for a WO$_3$ cluster containing 12 W atoms using ADF with BP functionals and a TDZ basis set, taking the atoms nearest the centre of the cluster as best representative of bulk WO$_3$.

The other contribution to the energetic difference near the interface is the change in the dielectric properties that govern the electrostatic energy. We have shown previously [27] that this is accurately reproduced up to a few atom spacings from the interface by an image-charge mechanism, taking account of the difference in static electric permittivity between the polymer material and the tungsten oxide. However, it proves inconvenient to use this approach with our method for simulation of the ion motion, and so we model the same contribution by a polarization energy term. To lowest order, the polarization energy between two atoms i and j with polarizabilities α_i and α_j separated by a distance r is given by

$$U_{ij} = -\frac{q_i^2 \alpha_j + q_j^2 \alpha_i}{r} \tag{3}$$

The atomic partial charges and low-frequency polarizabilities for the species in PEO are available in the literature, as is the polarizability of O^{2-} [28], taken as the anion species in WO$_3$. By analysing polarizabilities for a series of complex crystalline oxide and fluoride species containing tungsten [29], assuming that their mean polarizability is a simple sum of the polarizabilities of the constituent ions, we derive an average polarizability volume of 4.24 Å^3 for the cation species W^{6+}.

We break the periodic boundary conditions of our model system along the x direction, and split the system into three regions, the oxide, the real polymer and the ghost polymer, as shown in Fig. 1. The oxide is a WO$_3$ structure tiled over $x > 0$ with all

atoms fixed as the lithium ion moves. The real polymer extends in the *yz* plane for a depth of one simulation cell below $x = 0$; its atoms are allowed to move during the simulation, but not into the other regions. Finally, the ghost polymer is a semi-infinite layer of fixed polymer below the real polymer for $x < 0$. Thus we freeze in the bulk configuration of the system except for the layer of polymer adjacent to the interface.
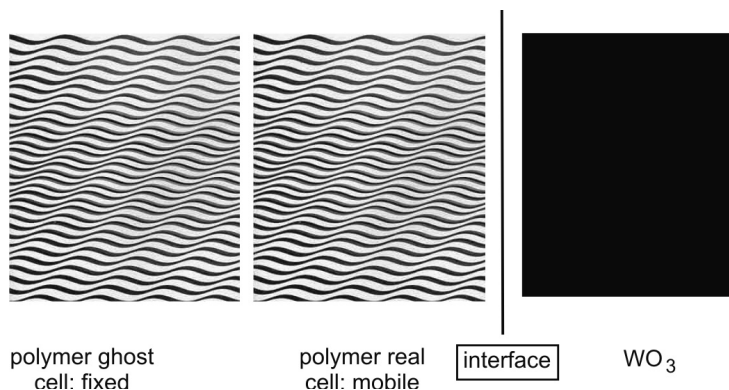

| polymer ghost | polymer real | interface | WO$_3$ |
| cell: fixed | cell: mobile | | |

Fig. 1. A scheme showing three regions used in simulating
the polymer and the interface to tungsten oxide

5. Simulation of transport

We simulate transport using an *n*-fold way kinetic Monte Carlo method described in detail elsewhere [30]. Each run comprises 20 000 steps, i.e. 400 for each of the 50 Li$^+$ ions in the simulation cell, with the structure of the real cell allowed to relax on the superimposed lattice after each move. Simulations are run at temperatures of 250 K, 300 K and 350 K, in zero field or in a field of 100 GV/m in the *x* direction; such a large field is used in order to achieve significant net motion of the ion during a simulation run of this relatively short duration, but we have verified that the transport remains linear up to this value. We perform simulations for the polymer alone and for the polymer with a tungsten oxide interface.

We find that during runs in the polymer alone, at 300 K in zero field Li$^+$ ions move 2–5 Å but in the field the ions move 35 Å along the direction of the field and 3–7 Å across it; these distances are higher at 350 K and lower at 250 K, as expected for an activated hopping process. Figures 2 and 3 show plots of the ion mean-square displacement during individual runs for fields in two perpendicular directions. These plots show spikes as an ion moves around exploring its immediate neighbourhood, interspersed with jumps as the ion moves to an adjacent neighbourhood. Jumps along the field are naturally favoured, though jumps across it can also be seen, and Figure 3 shows that jumps against the field are also possible. We have produced movies of ion trajectories that confirm this observation and show how moving against the field al-

lows an ion to circumvent a region where transport is hindered in order to move to a nearby region where transport along the field is easier.
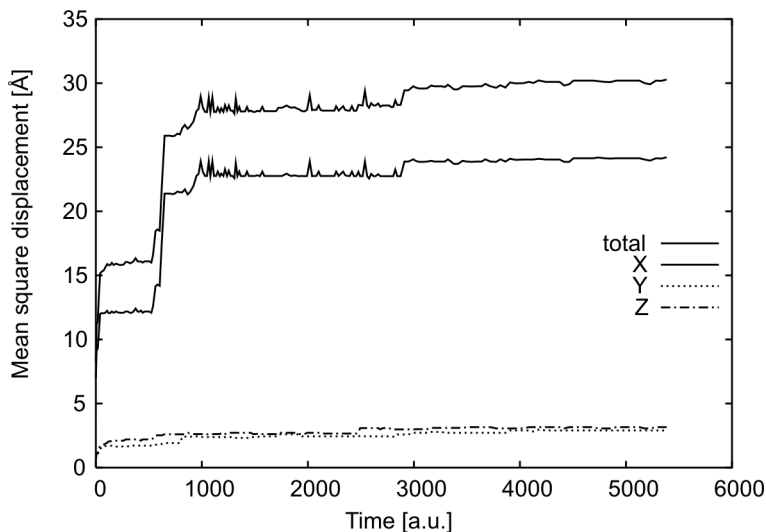

Fig. 2. Mean-square displacement of lithium ions
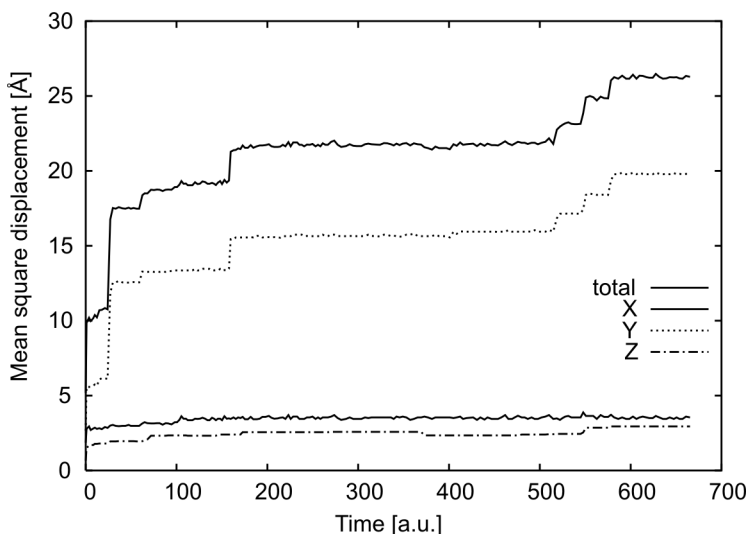in the polymer alone for a field in the *x* direction

Fig. 3. Mean-square displacement of lithium ions
in the polymer alone for a field in the *y* direction

During runs in the polymer with the tungsten oxide interface, the ions tend to ac-cumulate at the interface. This produces a repulsive potential for lithium ions at the interface, and significantly reduces their overall movement, with mean-square dis-

placements of only 5–6 Å, as shown in Figs. 4 and 5. This finding is consistent with calculations that model the process of lithium insertion into WO_3 films [15], which show that there are energy minima for a lithium ion on either side of the interface, which are of comparable depths when the polymer dielectric constant is included. Depth profiling measurements [31] also show that Li^+ does not readily penetrate into bulk WO_3.
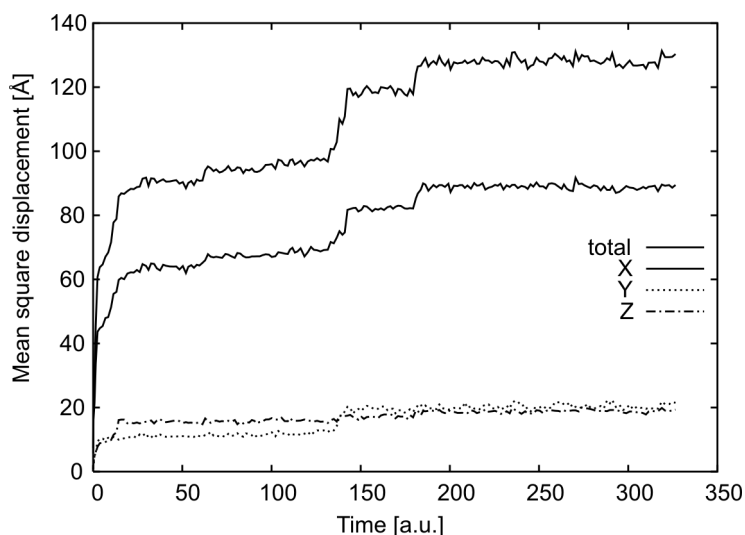

Fig. 4. Mean-square displacement of lithium ions in the polymer with the tungsten oxide interface for a field in the *x* direction, normal to the interface
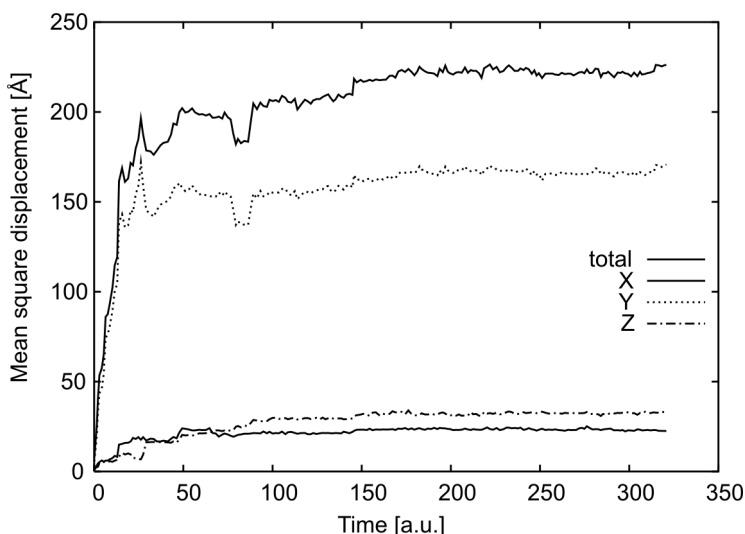

Fig. 5. Mean-square displacement of lithium ions in the polymer with the tungsten oxide interface for a field in the *y* direction, parallel to the interface

6. Conclusions

We have conducted Monte Carlo simulations of lithium ion transport in the polymer electrolyte system PEO–LiClO$_4$ both as the bulk material and with an interface to tungsten oxide. The simulations rely on a detailed model of the energetics including the Coulomb and polarization energies of the ions in the material. The picture that emerges is that ions 'rattle' in their local energy well, which is allowed to relax on a lattice to accommodate the ion motion, and occasionally 'hop' between adjacent wells. The same processes occur in an electric field, where ions may occasionally move against the field.

This shows that two timescales are involved in the motion, consistent with observations of two relaxation times in dielectric relaxation studies on poly(vinyl methyl ether)–LiClO$_4$ [12]. However, we also expect that ions 'slide' between wells on an even longer time scale as the polymer structure deforms; this is essentially the 'Red Sea event' mentioned in the Introduction, and corresponds to the microscopic process that underlies the dynamic bond percolation model [32]. Our simulation times are not long enough to show this behaviour, which is a standard problem that arises from the widely differing timescales of different processes in polymer materials. Our approach could be modified to explore these events by fixing the ions in position and allowing the polymer structure to evolve for a number of time steps, after which the ions are again allowed to respond to the new structure, and then repeating the sequence.

Overall, we have provided microscopic insights into the process of lithium ion transport on a realistic model of a practical polymer electrolyte–electrochromic system suitable for applications in glazing. The simulation process is kept simple in order to be practical for relatively routine use, but its various features have been validated against more detailed treatments. The approach is simple enough to be extended to other materials by relatively simple adjustments or computations of input parameters; for example, we have used it to explore the behaviour of systems in which PEO is replaced by variants with short side-chains designed to lower the glass temperature and enhance the ion mobility, and it could be used similarly to investigate the behaviour of systems with enhanced performance in which boronate esters replace PEO [33].

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