JOURNAL OF MATERIALS SCIENCE 30 (1995) 2296–2298

Ab initio self-consistent theory of ionic diffusion in superionic conductors with an internal interface

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The kinetic equation of the hopping diffusion in a one-dimensional chain with an internal interface between a superionic conductor and an intercalate, is presented in a new form, which explicitly takes into account the effect of Coulomb correlations. Numerical results are presented for material parameters corresponding to the system: ternary borate glass–indium selenide, which is often used in solid microbatteries.

1. Introduction

Many properties of materials in high-technology applications are strongly influenced by the presence of solid interfaces. An example is the solid interface of the disordered system–intercalate, and the study of its properties is important for the development of solid-state microbatteries, fuel cells and microsensors. The progress in this field has been reviewed recently [1]. Previous reviews of the general structural and transport properties of disordered materials and superionic conductors can be found elsewhere [2, 3].

In particular, the exploration of transport properties of one-dimensional disordered chains is of interest to a better understanding of the process of ion diffusion in substances such as glasses and superionic conductors. These materials have atomic arrangement with a relatively large degree of disorder and randomness. Being one-dimensional this model is relatively simple and the corresponding calculations are, in general, tractable in contrast to the much more complicated two- and three-dimensional cases.

For a theoretical description of ion diffusion across solid interfaces, the lattice–gas model is suitable. A model of this kind for a one-dimensional lattice with internal interface was proposed by Blender *et al.* [4]. Later, this model was generalized to include the interface energy [5], the random hopping rates in one of the sub-lattices, and also site-blocking [6], and the effect of Coulomb correlations [7].

In our previous work [7] we have demonstrated that it is necessary to take into account the Coulomb correlations in the theory of hopping diffusion. This makes the treatment more realistic, but non-linear and more difficult and time consuming to solve compared to the linear case [4, 5]. The major difficulty consists of the requirement to choose a very small time step when integrating the diffusion equation, and to account for the Coulomb correlations at every intermediate time step by modifying the self-consistent potential along the chain, which is obtained by solving the Poisson equation. In this way, self-consistent solutions for the ion density and the potential can be obtained, but it is difficult to control the error of the solution, which usually increases with diffusion time. The object of this paper is to present a new formulation of the kinetic equation of the hopping diffusion along a one-dimensional chain, which will be self-consistent, accurate and numerically tractable for all diffusion times.

2. The kinetic equation

Consider a one-dimensional chain with N points and an internal interface. The general form of the kinetic equation, which describes the hopping diffusion of ions along this chain is given by

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_j \left[b_{ij} n_i (1 - n_j) - b_{ji} n_j (1 - n_i) \right] \qquad (1)$$

where n_i is the ion density, the subscripts i, j denote configurations and b_{ij} are hopping rates, which are assumed to fulfil the conditions for detailed balance $b_{ij} = b_{ji}$.

The kinetic equations resulting from the lattice–gas model of hopping diffusion along the chain, when one starts from some initial distribution, are given by Equations 1–3 in [4]. The effect of the Coulomb correlations is included in the formalism through the solution of the Poisson equation, as described by Nachev and Balkanski [7]. Here, a new form of the kinetic equation is proposed, which explicitly takes

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into account the effect of the Coulomb correlations. This equation replaces Equations 1–3 in [4], and is given by

$$\frac{dn_1}{dt} = b_2 n_2(1 - n_1)\exp(\gamma_r n_1) - b_1 n_1(1 - n_2)\exp(-\gamma_r n_1) \qquad (2a)$$

$$\begin{aligned}\frac{dn_i}{dt} = {} & b_{i-1}n_{i-1}(1 - n_i)\exp\left(-\gamma_r \sum_{j=1}^{i-1} n_j\right) \\ & - b_i n_i(1 - n_{i-1})\exp\left(\gamma_r \sum_{j=1}^{i-1} n_j\right) \\ & + b_{i+1}n_{i+1}(1 - n_i)\exp\left(\gamma_r \sum_{j=1}^{i} n_j\right) \\ & - b_i n_i(1 - n_{i+1})\exp\left(-\gamma_r \sum_{j=1}^{i} n_j\right) \\ & (i = 2,\ldots N - 1) \qquad (2b)\end{aligned}$$

$$\begin{aligned}\frac{dn_N}{dt} = {} & b_{N-1}n_{N-1}(1 - n_N)\exp\left(-\gamma_r \sum_{j=1}^{N} n_j\right) \\ & - b_N n_N(1 - n_{N-1})\exp\left(\gamma_r \sum_{j=1}^{N} n_j\right) \qquad (2c)\end{aligned}$$

where the subscript i denotes a site of the lattice, n_i is the ion concentration along the chain and b_i are the hopping rates between two lattice sites, which are first neighbours. Part of b_i could be random in the glassy part of the chain. When deriving the kinetic Equation 2a–c it was assumed that the hopping rates depend exponentially on the barrier height and on the inverse temperature in Arrhenius form.

A factor g_r, which depends on the material parameters and which has different values on both sides of the interface ($r = 1, 2$), can be defined as

$$g_r = \frac{e^2 d_r^2}{2k_B T \varepsilon_0 \varepsilon_r} \qquad (3)$$

where

$$\varepsilon_r = \begin{cases} r = 1: & \varepsilon_{glass}\ (i = 1, \ldots, N_{int}) \\ r = 2: & \varepsilon_{InSe}\ (i = N_{int} + 1, \ldots, N) \end{cases}$$

and the interface is between lattice sites N_{int} and $N_{int} + 1$.

When the ion concentration n_i along the chain is considered as the occupation probability of the corresponding site i ($i = 1, \ldots, N$), then the factor g_r in Equation 3 is dimensionless and is given by the following expression, used in Equation 2a–c

$$\gamma_r = \frac{e^2}{2k_B T \varepsilon_0 \varepsilon_r d_r N^3} \qquad (4)$$

The site-blocking effect is accounted in Equations 1 and 2 through the factors $(1 - n)$ and the other symbols have their usual meaning: e is the elemental charge, T is the temperature, k_B is the Boltzmann constant, d is the average distance between two sites of the chain and the absolute and relative permeability are denoted by ε_0 and ε_r, respectively. Reflecting boundary conditions on the left ($i = 1$) and right ($i = N$) edges of the chain are assumed in the kinetic Equation 2a–c.

3. Numerical results and discussion

The material parameters in our numerical examples will be specified for the solid interface between a ternary borate glass and indium selenide. The hopping rates in these materials can be obtained by dielectric loss measurements and overvoltage measurements, respectively, as described elsewhere [1, 8]. From these measurements, the hopping rates in lithium-doped ternary borate glass B_2O_3–$0.5Li_2O$–$0.15Li_2SO_4$ are estimated to be $\alpha \approx 3 \times 10^4\ s^{-1}$ for $T = 460$ K. The hopping rates in lithium-doped indium selenide Li_yInSe are estimated to be 10^4–$10^7\ s^{-1}$ for $y = 0$–1. Therefore, we can denote the hopping rates in the glass by $b_i = \alpha\ (1 + \eta r_i)$, where r_i are random numbers in the range (0–1) and $|\eta| < 1$ is a factor, which controls their magnitude around α. The hopping rates in the intercalate Li_yInSe will be considered as constant: $b_i = \xi\alpha$, where ξ is a parameter of the model. The relative dielectric constants in Equations 3 and 4 are $\varepsilon_{glass} = 7.4$ and $\varepsilon_{InSe} = 8.5$ [8] and $d_1 \approx d_2 = 0.4$ nm [9].

Solutions of the kinetic Equation 2a–c are plotted in Fig. 1 for $\varepsilon = 6$, $\eta = 0.05$ and different diffusion times $t = 0$, $500\Delta t$, $1000\Delta t$ and $1500\Delta t$. The time step Δt for the integration of Equation 2a–c is specified to be $\Delta t = 5 \times 10^{-7}\ s^{-1}$. The initial distribution at $t = 0$ is step-like right at the interface. The diffusion profiles for higher times ($t > 0$) are asymmetric around the interface because of the different material parameters – mainly the values of the hopping rates. One can also study solutions on the kinetic Equation 2 for other initial distributions, but the step-like distribution was chosen here because it corresponds to the real case when lithium ions diffuse from doped ternary borate glass to the intercalate InSe in the cathode of a solid microbattery.

The time dependence of the edge ion concentration $n_{i=N}(t)$ on the right side of the chain is an important function because it shows how ions diffuse through thin films. This is plotted in Fig. 2 for relatively long

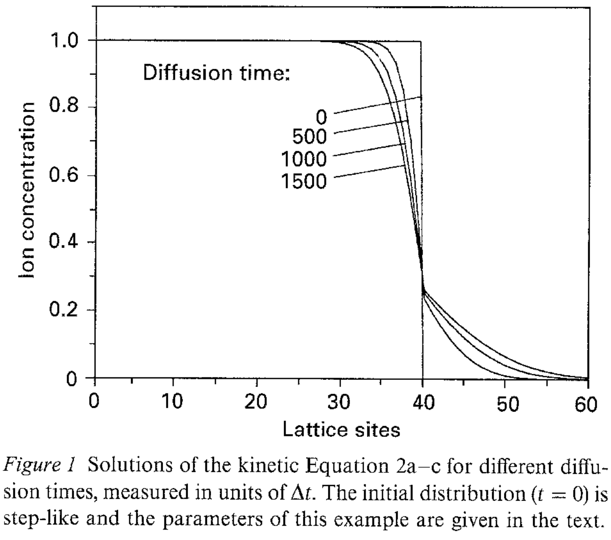

Figure 1 Solutions of the kinetic Equation 2a–c for different diffusion times, measured in units of Δt. The initial distribution ($t = 0$) is step-like and the parameters of this example are given in the text.

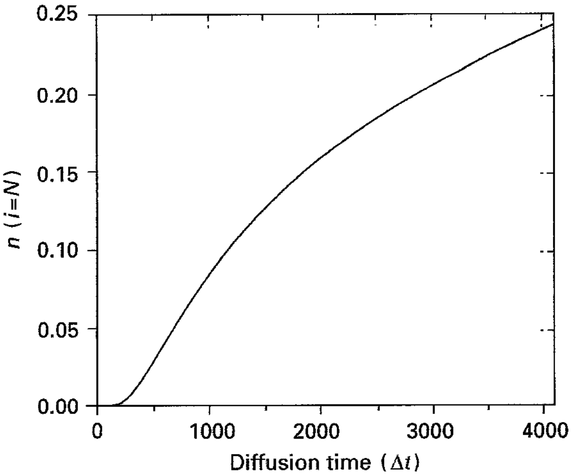

Figure 2 The time dependence of the edge ion concentration $n_{i=N}(t)$ for $\xi = 7$, $N = 60$ and $\eta = 0.05$. The diffusion time is measured in units of Δt.

diffusion time, which is measured in units Δt. Owing to the reflecting boundary conditions imposed on the kinetic Equation 2a–c, this curve will saturate asymptotically ($t \rightarrow \infty$) to the mean ion concentration.

In summary, a new form of the kinetic equation of the hopping diffusion of ions in one-dimensional chain with internal interface is proposed. This form is *ab initio* self-consistent for all diffusion times. Numerical solutions of this equation are presented, which model the transport of lithium ions across a material interface in a solid microbattery. The software, used in the present simulations, is written on FORTRAN 77 and is available upon request.

Acknowledgements

One of us (I.N.) thanks Professor Sir R. J. Elliott and Dr R. Barrio for clarifying discussions. The work presented in this paper was funded by EEC Contract CI1-CT90-0864.

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Received 9 March
and accepted 14 November 1994