Numerical simulation of ion distribution in polymer electrolytes with blocking electrodes

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ABSTRACT

A numerical procedure is introduced to calculate the profiles of ion densities and electric fields in polymer electrolytes with blocking electrodes. For low electric potentials the numerical results are in agreement with Jaffé's approximate analytical solutions. In contrast to the analytical solution the numerical procedure is also suitable for high electric potentials at which the relation between dielectric polarisation and electric potential becomes strongly nonlinear. Furthermore, the temporal development of ion distributions can be modelled after the application of a voltage step or under other transient voltages.

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1. Introduction

Polymer electrolytes are of significant technological interest because of their potential for use in batteries, membranes for fuel cells, and sensors. With suitable combinations of polymers and an alkaline salt a solid-like electrolyte with sufficient ionic conductivity may be produced [1]. It is believed that understanding the ionic transport mechanism will aid the optimisation of future polymer systems [2]. For this reason the motion of ions in a polymer matrix is a very interesting topic.

Ionic motion shows effects in the low frequency region, where moving ions contribute significantly to the overall current during one half-period of a harmonic excitation. For this reason, studying conduction at such frequencies and comparing with theory is an important tool. In the present work, a numerical calculation for time dependent ion distributions under external electric potentials is introduced.

2. Theory

Moveable ions in polymer electrolytes are often unable to cross material-electrode boundaries. If low frequency voltages are applied on the electrodes, large concentrations of ions develop near those interfaces. This effect was firstly treated theoretically based on Maxwell's theory by Wagner [3] and Sillars [4], leads to large dipole moments since oppositely charged ions propagate to opposite ends of the sample.

The ions' distribution in a homogeneous material in such cases is a result of drift and diffusion and, assuming a constant number of ions, is described in one dimension by Jaffé G [5]:

$$\frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2} - \mu_p \frac{\partial}{\partial x}(pE) \tag{1}$$

$$\frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} + \mu_n \frac{\partial}{\partial x}(nE) \tag{2}$$

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$$\frac{\partial E}{\partial x} = \frac{e}{\varepsilon}(p - n). \tag{3}$$

Here p and n are densities of positive and negative ions, μ_p, μ_p and D_p, D_n their mobilities and diffusion coefficients, E electric field, e elementary electric charge, and ε permittivity of the material. ε includes the contributions from electronic, ionic and orientational polarisation, but not of space—charge (or electrode interfacial) polarisation. It is therefore related to the capacitance of the polymer electrolyte at frequencies above the reciprocal relaxation time of space—charge polarisation. To keep the formulae short we assume that each positive ion carries charge e and each negative ion charge $-e$. In case that the positive ions and negative ions carry the charges $z_p e$ and $-z_n e$, p and n in all equations of this paper have to be replaced by $z_p p$ and $z_n n$, respectively.

The assumption that ions can move freely in the medium, but cannot transport charge through the electrode-electrolyte interfaces implies that the current vanishes at the positions of the electrodes. For a plate-like sample of thickness L with electrodes located at $x = 0$ and $x = L$ this finds expression in the boundary conditions:

$$\left. \begin{array}{l} D_p \frac{\partial p}{\partial x} - \mu_p p E = 0 \\ D_n \frac{\partial n}{\partial x} + \mu_n n E = 0 \end{array} \right\} \text{for } x = 0 \text{ and } x = L. \tag{4}$$

The electric potential between the electrodes is given by

$$U = \int_0^L E dx. \tag{5}$$

3.   Solution for static conditions

For static externally applied voltages, the set of equations above is analytically solvable if the quotient of diffusion coefficient and mobility is the same for positive and negative ions ($D_p/\mu_p = D_n/\mu_n$), i.e. under the very general Einstein conditions:

$$\mu_p = D_p e/(k_B T), \tag{6}$$

$$\mu_n = D_n e/(k_B T), \tag{7}$$

from which follows:

$$\mu_p/D_p = \mu_n/D_n = e/(k_B T). \tag{8}$$

Jaffé has introduced reduced (dimensionless) ion densities p_{red} and n_{red}, coordinate x_{red}, sample thickness L_{red} and electric field E_{red} to integrate Eqs. (1)—(3) with the boundary conditions in Eq. (4) for the stationary case with a constant voltage between the electrodes [5]. With the assumption in Eq. (8) and under the conditions that the mean densities p_0 and n_0 of the positive and negative ions in the sample are equal and that no generation or recombination of ion pairs takes place, the reduced (dimensionless) ion densities p_{red} and n_{red}, coordinate x_{red}, sample thickness L_{red}, electric field E_{red} and voltage between the electrodes U_{red} have the following form:

$$p_{red}(= \pi) = p/p_0 = \sqrt{p/n} \tag{9}$$

$$n_{red}(= \nu) = n/p_0 = p_0/p = \sqrt{n/p} \tag{10}$$

$$x_{red}(= \xi) = \sqrt{\frac{e p_0}{\varepsilon} \frac{\mu_p}{D_p}} x = \sqrt{\frac{e^2 p_0}{\varepsilon k_B T}} x \tag{11}$$

$$L_{red}(= \delta) = \sqrt{\frac{e p_0}{\varepsilon} \frac{\mu_p}{D_p}} L = \sqrt{\frac{e^2 p_0}{\varepsilon k_B T}} L \tag{12}$$

$$E_{red}(= \eta) = \sqrt{\frac{\varepsilon}{e p_0} \frac{\mu_p}{D_p}} E = \sqrt{\frac{\varepsilon}{k_B T p_0}} E \tag{13}$$

$$U_{red}(= 2V') = \frac{\mu_p}{D_p} U = \frac{e}{k_B T} U \tag{14}$$

All the equations have been converted to the SI unit system. The symbols used in Ref. [5] are given in round brackets in the equations above. p_0 and n_0 are the mean concentrations of positive and negative ions in the sample. For the case that the space charge regions are limited to relative thin layers at the electrodes, Jaffé has derived the following expression for the reduced ion distributions $p_{red}(x_{red})$ and $n_{red}(x_{red})$ for positive and negative ions and for the reduced electric field $p_{red}(x_{red})$, that develop in a disk-shaped sample of a medium with blocking electrodes when a static voltage is applied on the electrodes ($-L_{red}/2 \leq x_{red} \leq L_{red}/2$) [5]:

$$p_{red} = \frac{1}{n_{red}} \approx \frac{1 + (E_{0,red}/\sqrt{8})\sinh(\sqrt{2} \, x_{red})}{1 - (E_{0,red}/\sqrt{8})\sinh(\sqrt{2} \, x_{red})} \tag{15}$$

$$E_{red} \approx \frac{E_{0,red}\cosh(\sqrt{2} x_{red})}{1 - (E_{0,red}^2/8)\sinh^2(\sqrt{2} x_{red})} \tag{16}$$

with $E_{0,red}$ the reduced electric field in the centre of the sample:

$$E_{0,red} = \sqrt{8} \, \frac{\tanh(U_{red}/4)}{\sinh(L_{red}/\sqrt{2})} \tag{17}$$

or

$$p(x) = \frac{p_0^2}{n(x)} \approx p_0 \left[\frac{1 + \sqrt{\frac{\varepsilon}{8 k_B T p_0}} E_0 \sinh\left(\sqrt{2 \frac{p_0}{\varepsilon k_B T}} e x\right)}{1 - \sqrt{\frac{\varepsilon}{8 k_B T p_0}} E_0 \sinh\left(\sqrt{2 \frac{p_0}{\varepsilon k_B T}} e x\right)} \right] \tag{18}$$

with

$$E_0 = \sqrt{8} \, \frac{\tanh\left(\frac{eU}{4 k_B T}\right)}{\sinh\left(\sqrt{\frac{p_0}{4 \varepsilon k_B T}} e L\right)}. \tag{19}$$

Eqs. (15)—(19) describe an approximate solution for the case, that charges accumulate in regions close to the electrodes i.e., for low electric fields. Fig. 2 shows a plot of the reduced charge density of the positive ions as a function of location for different voltages calculated with Eq. (15). The distribution of the negative ions can be found by mirroring the distribution of positive ions on a plane located halfways between the electrodes. Fig. 3 shows the profiles of the corresponding electric fields after Eq. (16).