

## Charge Distribution Around Nanoscale Nonhomogeneities in Solid State Ionics

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The system of Nernst-Planck-Poisson equations is modified by including the gradient terms in the chemical potential expression. The gradient terms are important in the regions of significant inhomogeneities, e. g. near the interface boundaries. These modified equations are used for investigating the particle density distribution in the vicinity of interphase boundary of a solid electrolyte. The differential equation of the fourth order for the problem of contact between two solid phases is formulated. Its analytic solution which describes non monotonic distribution of charge in both phases is obtained. It is shown that the gradient component added in the transport equations makes a decisive contribution in the double layer region. The approach is further expanded to the system composed of bulk phases and the intergrain layer between them. The particle density distributions at different conditions are investigated. The quasi-one dimensional lattice model of the fuel cell is considered in the frame of kinetic Monte Carlo simulation. It is shown that the electrostatic interaction between ions makes a significant contribution to the activation energy of migration of the particles. On the other hand, the fluctuations of the energy barriers slightly increase the particle migration activation energy. It is found that at blocked electrodes in the near electrode regions electrical double layers are formed. The thickness of the electrical double layer is around few lattice constants.

**Keywords:** Nernst-Planck-Poisson equations, Solid state ionics, Fuel cell, Lattice model, Kinetic Monte Carlo, Charge density, Electric conductivity, Transition probability, Activation energy.

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### 1. INTRODUCTION

Solid state ionics are widely used in fuel cells, chemical sensors, capacitors, current sources etc. They are characterized by high electric charged particle concentration and thus nanoscale density variations around of any spatial nonhomogeneity such as intergrain or interphase boundary. These charge density variations significantly influence electric conductivity and other characteristics of the devices where solid state ionics are used.

The system of Nernst-Planck-Poisson (NPP) equations is widely used for investigating the electromigration mechanisms in various cases [1, 2]. The linearized NPP equations can describe the basic mechanisms of charge transport in the solid-state electrochemical systems and are convenient means for analytical considerations. In accordance with these equations the total flux of particles in the medium is determined by the gradient of the electrochemical potential and consists of two components generated by the driving forces proportional to the gradients of the electric potential and the concentration of particles that leads to the differential equations of the second order. This approach is successful in analyzing the migration of particles within a single phase with a small nonhomogeneity of the density distribution over the volume of the system and cannot be used in more complex cases of interface boundaries when the double layer structures require non monotonic particle density distribution on the nanometer scale. In the latter case the density gradient contribution to the free energy and the chemical potential is quite important and leads to differential equations of the fourth order that describe a nonuniform particle density distribution more consistently.

Nonlinear versions of the NPP equations can hardly be solved analytically. For numerical investigation molecular dynamics (MD) and kinetic Monte Carlo (KMC) are more suitable methods because they give possibility more closely address physical nature of the systems under investigation. The former can be used to simulate the systems of the order of  $10^5$  atoms on time scales of the order of tens nanoseconds and requires more processing power. However, a large number of important processes occur on a time scale much longer than nanosecond range and KMC tools are better suited for studying such phenomena. Thus, analytical and KMC methods are used below for describing the particle and charge distribution variations on nanoscale.

### 2. GRADIENT CONTRIBUTION TO THE FREE ENERGY AND CHEMICAL POTENTIAL

#### 2.1 Constitutive Equations

When the system is nonhomogeneous in  $x$  direction a common representation [3, 4] of the free energy  $F$  through the deviation  $\delta\rho(x)$  of the density field  $\rho(x)$  from its homogeneous value can be written as follows:

$$F = \int_{-\infty}^{\infty} \left( f(\rho(x)) - \alpha (\partial\delta\rho/\partial x)^2 \right) dx, \quad \alpha < 0, \quad (2.1)$$

where  $f(\rho(x))$  is the free energy density of the equilibrium homogeneous system of constant density  $\rho$ , which is equal to the density  $\rho(x)$  of the nonhomogeneous system at position  $x$ . The second term under the integral represents the density gradient contribution. After integration of this equation by parts we get:

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$$\delta F = \int_{-\infty}^{\infty} \left( \frac{\partial f(\rho(x))}{\partial \rho} + \alpha \frac{\partial^2 \rho}{\partial x^2} \right) \delta \rho(x) dx \quad (2.2)$$

that results in the expression for the chemical potential

$$\mu(x) = \frac{\partial f(\rho(x))}{\partial \rho} + \alpha \frac{\partial^2 \rho}{\partial x^2}. \quad (2.3)$$

The first summand in the right hand side coincides with the electrochemical potential of a homogeneous medium and thus

$$\mu(x) = \mu_{ch}(x) + q\varphi(x) + \alpha(\partial^2 \rho / \partial x^2), \quad (2.4)$$

$\mu_{ch}$  is the chemical potential,  $q$  the particle charge,  $\varphi$  the electric field potential. The last summand is an important contribution originating from the gradient term in the free energy expression.

For the system of two solid phases with plane interface at position  $x = 0$  the condition of thermodynamic equilibrium can be written as a generalized NPP equation

$$\mu_{ch}(x) + q\varphi - \frac{\alpha \varepsilon}{q} \frac{\partial^4 \varphi}{\partial x^4} = \mu_{ch}(\rho_j) + \text{sgn}(x)qu, \quad j = 1, 2 \quad (2.5)$$

$$\varphi(x) = \text{sgn}(x)u \left( 1 + \frac{k_1^2}{k_2^2 - k_1^2} \exp(-\text{sgn}(x)k_2x) - \frac{k_2^2}{k_2^2 - k_1^2} \exp(-\text{sgn}(x)k_1x) \right), \quad k_{1,2} = \sqrt{\frac{-\gamma}{2\alpha} \pm \sqrt{\left(\frac{\gamma}{2\alpha}\right)^2 + \frac{q^2}{\alpha\varepsilon}}}, \quad \gamma_1 = \gamma_2 = \gamma. \quad (2.10)$$

The charge density distribution following from this solution clearly indicates the occurrence of the double layer in the vicinity of the interface.

## 2.2 The Particle Density Distribution at Interface and Intergrain Layers

The solution (2.10) can be directly applied to the double layer problem at the interface of an ionic electrode and electrolyte. In accordance with the Poisson equation double integration of this solution determines the charge density distribution with two extremes at

$$x_{1,2} = \pm \frac{\ln(k_2/k_1)}{k_2 - k_1}. \quad (2.11)$$

For simplicity it is supposed that the physical characteristics of both phases are identical ( $\gamma, \varepsilon, \alpha$  are the same for both phases). It should be noted that without the terms containing  $\alpha$  it is not possible to reproduce the peculiar features of the double layer structure.

The charge density distribution in the system containing two plain blocking electrodes and thick electrolyte between them is shown in Fig. 2.1. The two double layers are clearly seen with two extremes each.

The approach developed can be applied for the case of intergrain boundary layer. The model system consists of three layers: two bulk phases and the intergrain layer between them. The latter is characterized by an additional electric potential originating from microscopic interparticle interactions. Then the generalized NPP equation can be represented as the system of three differential equations of the fourth order for three different layers. If the intergrain boundary is thin enough the charge distribution at zero total potential

with the symmetrized boundary conditions

$$\varphi(-\infty) = -u, \quad \varphi(+\infty) = +u, \quad \varphi(0) = 0. \quad (2.6)$$

Here  $\mu_{ch}(\rho_1)$  and  $\mu_{ch}(\rho_2)$  are the equilibrium chemical potentials of the left and right hand phases far from the interface boundary,  $2u$  is the contact potential difference of the solids (the total potential difference),  $\varepsilon$  is the medium dielectric constant.

The chemical potential can be represented through the variation of density

$$\mu_{ch}(x) = \mu_{ch}(\rho_j) + \gamma_j \delta \rho_j(x), \quad (2.7)$$

with the thermodynamic factors

$$\gamma_j = \partial \mu(\rho_j) / \partial \rho_j, \quad j = 1 \text{ or } 2 \text{ for } x < 0 \text{ or } x > 0. \quad (2.8)$$

The constitutive equation acquires the form

$$\frac{-\gamma \varepsilon}{q} \frac{\partial^2 \varphi}{\partial x^2} + q\varphi - \frac{\alpha \varepsilon}{q} \frac{\partial^4 \varphi}{\partial x^4} = \text{sgn}(x)qu. \quad (2.9)$$

The particle density distribution follows from the solution of this equation

difference is symmetric and contains the only extreme in the region of the intergrain boundary and two extremes in the regions of the plains separating the grain bulks and intergrain boundary (Fig. 2.2).

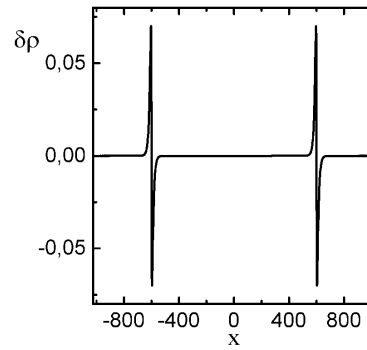


Fig. 2.1 – Charge distribution in the cell with blocking electrodes

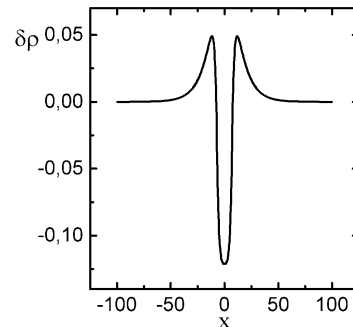


Fig. 2.2 – Charge distribution in the region of thin intergrain boundary

In the case of thick intergrain boundary the central extreme breaks down into two extremes with a flat part between them for significantly wide intergrain layer. In the general case of nonzero intergrain and total potential difference the charge distribution is more complicated.

### 3. DISTRIBUTION OF CHARGES IN QUASI-ONE-DIMENSIONAL MODEL OF A FUEL CELL

#### 3.1 The Model

Yttria-Stabilized Zirconia (YSZ) cells are widely used in different electrochemical devices [5-7]. The simplest configuration, the quasi-one-dimensional model [8], that allows us to perform relatively simple calculations is considered below. Fig. 3.1 shows the simplified cell structure for the YSZ electrolyte as an example of this model.

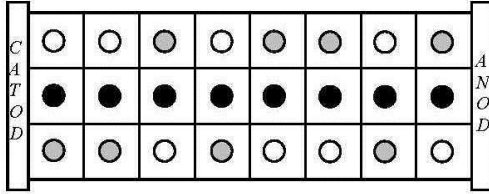


Fig. 3.1 – A one-dimensional lattice for the KMC model

The volume of each unit cell (shown as a column divided into three parts) contains one vacancy (open circle) when no external potential is applied. Each cell has two locations for the negative ions (open and gray circles) and one location for positive ions (black circles), and after doping there is one negative and one positive ion per unit cell, leaving one vacancy. The positive ions (Y) are considered to be fixed and the negative ions (O) can jump from one cell to the other, under the influence of an electric field or due to thermal fluctuations. The oxygen ions can jump to the right or left nearest neighbor unit cell when the latter contains one vacancy at least.

#### 3.2 KMC Simulation Procedure

In KMC simulation the rate of particle jumps due to thermally activated processes is modeled via an Arrhenius type expression for the jump frequency

$$P = P_0 \exp(-\varepsilon_a/k_B T) \quad (3.1)$$

where  $P_0$  is a pre-exponential factor,  $T$  the temperature and  $k_B$  the Boltzmann constant. The activation energy  $\varepsilon_a$  consist of activation energy of bulk diffusion  $\varepsilon_{BD}$  and the electrical contribution  $\varepsilon_F$ .

$$\varepsilon_a = \varepsilon_{BD} + \varepsilon_F, \quad (3.2)$$

To account for the nonuniform distribution of activation energy, with which can be modeled, for example, the influence of nonhomogeneities or defects in the system or the grain boundaries in the electrolyte, the value of interstitial energy barrier can be represented as

$$\varepsilon_{BD} = \varepsilon_0 + \delta\varepsilon, \quad (3.3)$$

where  $\varepsilon_0$  is the average value of the barrier,  $\delta\varepsilon$  is its

variation, which obeys some special requirements. Below it is considered as a random variable with a uniform distribution in some energy range

$$\varepsilon_{BD} = \varepsilon_0 + 2\delta\varepsilon(x_r - 0.5), \quad (3.4)$$

where  $x_r$  is uniformly distributed pseudo-random number in the interval from 0 to 1.

The electrical contribution to the activation energy is defined by the expression [8]

$$\varepsilon_F = \alpha_0 q (U + E_{ion} + E_{cell}), \quad (3.5)$$

where  $q$  is the charge of moving ion,  $\alpha_0$  the lattice spacing,  $U$  the external electric field,  $E_{ion}$  the contribution to the total electric field from the fixed and mobile ions within the electrolyte. The term  $E_{cell}$  is the electric field imposed on the charge being moved by the ionic charges on the same sheet that are not being moved.

The ionic electric field at site  $j$  is computed in the approximation that the total charge of all the equivalent cells belonging to a sheet perpendicular to the fuel cell axes is uniformly distributed over the sheet area. Then the electric field can be computed by summing over all the possible charge sheets. A net positive charge on sheet  $k$  has a positive contribution to the ionic field if  $k < j$ , and a negative contribution if  $k > j$ . The ions associated with sheet  $j$  do not contribute to the electric field of that sheet. Therefore:

$$E_{ion}(j) = \frac{1}{2\varepsilon} \left( \sum_{k=1}^{j-1} Q(k) - \sum_{k=j+1}^N Q(k) \right), \quad (3.6)$$

where  $\varepsilon$  is permittivity,  $Q(k)$  is charge of  $k^{\text{th}}$  sheet. The work required to move an ion on sheet  $j$  which must account for the charges on that sheet other than the charge being moved. This contribution is determined by calculating the electric field,  $E_{cell}$  sheet, due to these charges

$$E_{cell}(j) = \pm \frac{1}{2\varepsilon} (Q(j) - q), \quad (3.7)$$

where plus / minus correspond a charge moves to sheet  $j \pm 1$ , respectively.

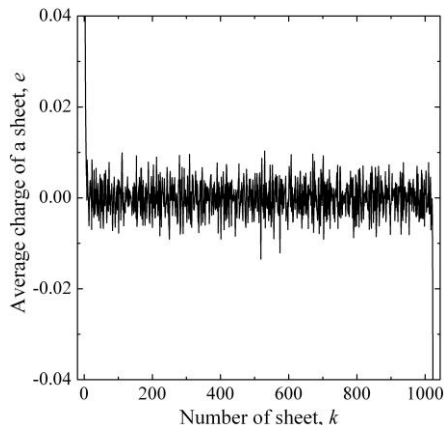
For modeling the movement of oxygen ions in the lattice we used the next physical parameters. External electric field is assumed to be  $U = 10^6 \text{V/m}$ . The lattice spacing is  $a_0 = 0.737 \text{ nm}$  in accordance with [8]. Then the interaction constant for doubly charged ions of oxygen is  $2e^2/\varepsilon_0\varepsilon a = 0.784 \times 10^{-19} \text{ J}$ , where  $e$  is the electron charge,  $\varepsilon_0$  the electric constant. The permittivity of the medium  $\varepsilon = 100$  adopted taking into account the partial screening by the electron subsystem of the solid electrolyte.

Simulations were performed for the lattice containing  $2^{10}$  sheets. The simulation procedure consists of  $1.01 \times 10^6$  MC steps. The first  $10^4$  steps designed for the transition of the system to an equilibrium state and were not taken into account in the averaging of the simulation results. The lattice barriers were rearranged after every 100 steps in accordance with Eq. (3.4).

#### 3.3 Simulation Results

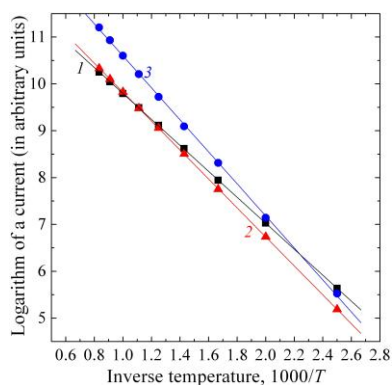
The consideration of a "closed" system, in which ions cannot move across the borders (at blocking elec-

trodes), gives possibility to study the distribution of the charges in the electrolyte in an external field at equilibrium. At high temperatures (Fig. 3.2). the average values of the sheet charges in the bulk of the system are close to zero, while double electric layers appear near the electrodes. The total charges in these layers and their widths are almost independent of temperature.



**Fig. 3.2** – Average charge of the sheets (in units of the electron charge) versus number of the sheet at high temperature ( $T \approx 800$  K)

The electric conductivity can be simulated at periodic boundary conditions. At applied external potential the number of particles moving through the system during a unit time is recorded. In Fig. 3.3 the dependence of the electric conductivity on the inverse temperature is shown for different values of the activation barrier fluctuations.



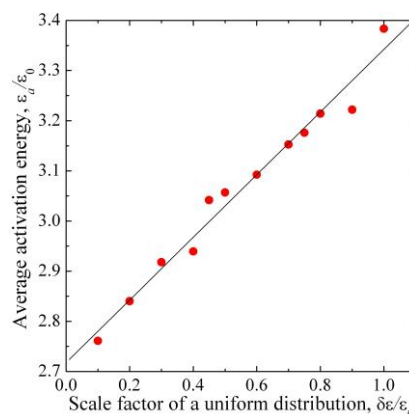
**Fig. 3.3** – Logarithm of the total charge passing through the electrolyte versus inverse temperature in the case of ordered lattice (curve 1, squares),  $\delta\varepsilon = 0.5$  (2, triangles) and  $\delta\varepsilon = 1.0$  (3, circles). The symbols represent the KMC simulation data, the solid lines are the results of the linear approximation.

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The values of the normalization constant  $P_0$  were determined in a series of test numerical experiments to optimize the simulation time and accuracy [8]. Finally all the data were reduced to common units which correspond to ordered lattice. The relation between the logarithm of the conductivity and the inverse temperature is practically linear that confirms the Arrhenius behavior for the conductivity at fluctuating activation barriers. The slopes of these lines determine the average activation energy of the model at different values of the parameter  $\delta\varepsilon$ . This dependence is approximately linear (Fig. 3.4) and can be represented by the expression

$$\varepsilon_a / \varepsilon_0 = 2.752 + 0.673\delta\varepsilon / \varepsilon_0, \quad (3.8)$$



**Fig. 3.4** – The average activation energy versus the scale coefficient of the uniform distribution

## 4. CONCLUSION

The gradient terms in the chemical potential expression result in modification of Nernst–Planck–Poisson equations and the possibility to reproduce the important features of the electric double layer structure. In the case of contact of two different ionic solids the double layer structure appears due to the contact potential difference of the solids. In the case of two bulk phases and the intergrain layer between them the density distribution is symmetric. The kinetic Monte Carlo simulation reveals the structure of the double layer and the electric conductivity of the electrolyte cell. The approach suggested can be used for a wide class of problems concerning electric field and particle density distributions in nonhomogeneous solid state ionics.

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