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Microscopic model of intergrain boundary junction

Vyacheslav Vikhrenko^{a*}, George Bokun^a, Antanas Orliukas^b, Tomas Šalkus^b

^aBelarsian State Technological University, Sverdlov Str 13a., Minsk BY-220006, Belarus

^bFaculty of Physics, Vilnius University, Sauletekio Av. 9/3, LT-10222 Vilnius, Lithuania

Abstract

The statistical mechanics differential-difference equations for the ions concentration distribution that account for the diffusion, electrical conductivity and Poisson contributions are derived. They represent differential-difference analogues of the phenomenological continuity equations for the ions. Spatial inhomogeneities (grain interiors, grain boundaries, intergrain regions, etc.) can easily be taken into account by proper adjusting the system material parameters (diffusion coefficients or particle transition rates, electric conductivities, thermodynamic factors or chemical capacitances). The solution of the equations allows investigating impedance spectra of inhomogeneous systems, e. g. electro-conducting ceramics. The results can be used for interpretation of experimental impedance spectra and evaluation of the medium transport characteristics. A simple example of the intergrain boundary junction is considered.

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1. Introduction

The significance of intergrain boundaries in solid electrolyte ceramics has been recognized since a long time ago, and many attempts to understand their influence on static and dynamic properties of ionic conductors were undertaken [1,2]. Impedance spectroscopy is widely used for investigation of dynamic properties [3] and interpretation of experimental results is usually based on equivalent electric circuit representations. However, electric circuits do not always reflect all important features of electrochemical systems, e. g. manifestation of

* Corresponding author. Tel.: +375 17 2924101.

E-mail address: vvikhre@gmail.com

chemical capacitances that can lead to uneven currents throughout the system or require using complex electric circuits [4].

Microscopic models are able to considerably improve our understanding of basic mechanisms of charge transport processes and the influence of space inhomogeneities on them. Molecular dynamics [5] as well as kinetic Monte Carlo [6,7] methods have demonstrated great potential in translating atomic-level information into experimentally observable properties. However, direct molecular dynamics and Monte Carlo simulations are excessively demanding with respect to computational resources, especially in case of inhomogeneous systems such as ceramic ionic materials. Considerable simplification of calculations can be achieved appealing to statistical mechanics information about lowest order particle distribution functions.

2. Microscopic equations and impedance spectra

We consider a system that consists of crystalline plains with lattice sites that can be occupied by mobile ions. Mobility of ions depends on the position of crystalline plains in the system and thus the plains belonging to grain interiors or to grain boundaries can be distinguished. The lattice fluid model can be used for description of transport phenomena in such a system.

It was previously shown [8,9] that the quasi-equilibrium thermally activated particle flux through the boundary between cells *i* and *j* can be written as

$$I_{ij} = v_{ij} (e^{\beta\mu_i} - e^{\beta\mu_j}) F(i, j), \quad v_{ij} = v_0 \exp(-u_{ij} / k_B T), \tag{1}$$

where *v* is the frequency factor, $\beta = 1 / (k_B T)$ is the inverse temperature, k_B is Boltzmann constant, *T* is the temperature, μ_i is the chemical potential at site *i*, *F*(*i*, *j*) defines the probability that two nearest neighbour lattice sites are unoccupied [10], *u_{ij}* is the activation energy for the transition between sites *i* and *j* in the limit of low concentration of diffusing species, *v*₀ is the attempt frequency of the order of 10¹² s⁻¹ [11].

For the system under consideration inhomogeneity is considered in one direction perpendicular to the crystalline plains. It is supposed that a small perturbation of external electric field is applied. Then the linearized expression for the flux from *i*-th to (*i*+1)-th crystalline plain can be written as

$$I_{i,i+1} = -v_{i,i+j} \exp(\beta\bar{\mu}) F(i, j) \beta (\mu_{i+1} - \mu_i - qhE_i), \tag{2}$$

where $\bar{\mu}$ is the equilibrium chemical potential, *q* is the ion charge, μ_i and *E_i* are the nonequilibrium deviation of the chemical potential from its equilibrium value and the electric field in *i*-th crystalline plane, *h* is the characteristic length (the lattice spacing). The term proportional to the electric field corresponds to the electrical conductivity, while the chemical potential contributions are due to the diffusion process.

The flux can be rewritten in terms of the ion concentration

$$I_{i,i+1} = -v_{ij} \exp(\beta\bar{\mu}) F(i, i+1) (\gamma_T / \bar{\rho})(\rho_{i+1} - \rho_i) - \beta q E_i h, \quad \gamma_T = \bar{\rho} (\partial(\beta\bar{\mu}) / \partial\bar{\rho}), \tag{3}$$

where $\bar{\rho}$ is the equilibrium dimensionless concentration of ions (the occupation number), ρ is the concentration deviation from its equilibrium value, γ_T is the thermodynamic factor.

The electric field is approximately calculated as the field created by the crystal planes with homogeneously distributed charges

$$E_i = qQ_i / (\epsilon\epsilon_0 h^2), \quad Q_i = 0.5 \sum_{k=1}^i \rho_k - \sum_{k=i+1}^n \rho_k, \tag{4}$$

where ϵ is the medium dielectric constant, ϵ_0 is the electric constant, *n* is the total number of the crystal planes in the system and the plains are numbered from the left to the right hand side of the system, for example.

The final expression for the flux within homogeneous layers of ceramics acquires the form

$$I_{i,i+1} = -D_i (\rho_{i+1} - \rho_i) - C_{iq} Q_i, \quad D_i = v_{ij} \exp(\beta \bar{\mu}) F(i, i+1) \gamma_T / \bar{\rho}, \quad C_{iq} = \beta q^2 \bar{\rho} / (\gamma_T \epsilon \epsilon_0 h), \quad (5)$$

where the microscopic expressions for the diffusion coefficient D_i and the chemical capacitance C_{iq} are introduced.

The time derivative of the concentration in i -th crystal plane is equal to the difference of the fluxes $I_{i-1,i} - I_{i,i+1}$, and after Laplace transform in case of a homogeneous system when the diffusion coefficient and the chemical capacitance are constant throughout the layer this equation takes the following form

$$i\omega \rho_i = D (\rho_{i-1} + \rho_{i+1} - 2\rho_i) - C_q \rho_i, \quad (6)$$

which can be considered as a differential-difference analogue and microscopic justification of the phenomenological continuity equation for the ions that accounts for the diffusion and Poisson (the last term) equations.

To take into account situations when the system contains layers with different characteristics (transition rates, diffusion and electric conductivity coefficients the concentration time derivative has to be directly calculated through difference of the fluxes

$$i\omega \rho_i = I_{i-1,i} - I_{i,i+1}, \quad (7)$$

where the fluxes are calculated in accordance with Eqs. (4) and (5) and thus the concentration distribution over the system directly enters to the right hand side of Eq. (7).

Having the solution of the last equation for the concentration distribution as a function of the plain position and frequency ω the impedance spectra can easily be calculated. It is possible to model systems with different distribution of material characteristics (diffusion coefficients and chemical capacitances or electrical conductivities) over the system.

In Fig. 1 the calculation results are shown. The system contains 3 layers. They represent two grain interiors with dimensionless coefficients $D_g=1000$ and $D_g C_g=1000$ and the intergrain boundary with coefficients $D_b=1$ and $D_b C_{bg}=1$ between them.

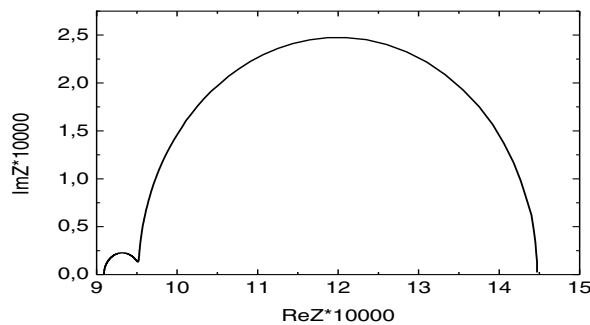


Fig. 1. Imaginary part (ImZ) of the impedans versus its real part (ReZ).

The contributions of the grain boundary (large semicircle) and the grain interiors (small semicircle) are clearly seen.

To simplify calculation we have used a quasi-one-dimensional model when inhomogeneity of the system and transport of ions occur in a particular direction while in planes perpendicular to this direction the system is considered to be uniform. Such simplification is frequently used in numerous investigations [12–14]. Of course, in real systems grain boundaries are distributed throughout the system in a complicated way. The solution of much simpler quasi-one-dimensional models can be used for this intricate problem.

On the other hand, for calculating the electric current from microscopic point of view it is necessary to consider jumps of particular ions over lattice site. These particular ions create in their vicinity specific distribution of other ions thus violating the assumption of uniformity in the perpendicular planes. The two-site distribution functions $F(i, j)$ entering Eq. (5) for fluxes can account for this uniformity.

3. Conclusion

The statistical mechanics derivation of the differential-difference equations for the ions concentration distribution that are the analogues of the phenomenological continuity equation for the ions that account for the diffusion, electrical conductivity and Poisson equations allow us to investigate impedance spectra of nonhomogeneous systems, e. g. electro-conducting ceramics. Although the proposed model is rather simplified its results can be used for interpretation of experimental impedance spectra and crude estimation of the important medium characteristics such as bulk and grain diffusion coefficients and chemical capacitances.

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