

Statistical description of electro-diffusion processes of ions intercalation in “electrolyte — electrode” system

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We propose a statistical theory of classical-quantum description of electro-diffusion processes of intercalation in “electrolyte — electrode” system. Using the nonequilibrium statistical operator method the generalized transport equations of Nernst-Planck type for ions and electrons in the “electrolyte — electrode” system are obtained. These equations take into account time memory effects and spatial heterogeneity. Within a classical description an analytical calculation of spatially inhomogeneous diffusion coefficients for ions is carried out.

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1. Introduction

Theoretical studies of electro-diffusion transport processes of ions and electrons in the “electrode — electrolyte” systems remain actual nowadays [1–7]. They are linked with a need to describe nonequilibrium processes of intercalation as well as to develop a theory suitable for practical application to predicting and controlling these processes. The difficulties in describing processes at electrode are first of all related with surface phenomena at electrolyte — electrode interface. In this region, complicated processes of adsorption and diffusion take place which are connected with a problem of charge accumulation at battery electrodes [8]. In the system “electrode (anode) — electrolyte — electrode (cathode)”, the anode plays role of the source of both electrons, which move to cathode by the corresponding electric circle, and lithium ions in electrolyte. A cathode is typically a metallic system (nickel, for example) covered with active material containing carbon and in which lithium ions intercalate from the solution. Herewith, an important issue is the following one. The electrochemical processes in electrolyte solution can be described using methods of classical statistical mechanics, whereas in the region near the electrolyte — electrode interface and inside the electrodes, description of diffusion and intercalation processes should be implemented by means of the modern methods of quantum statistical physics.

In this field, the electrochemical impedance studies [9–11] of electro-diffusion transport processes in Li-ion batteries [12–16] were carried out and intercalation/deintercalation processes were investigated using nonequilibrium thermodynamics [6,8,17–21]. In paper Ref. [8], it was proposed a generalized theoretical description of capacity loss and statistics on the battery lifetime from the viewpoint of formation of “electrolyte — electrode” interface near the negatively charged electrode is proposed. Basic

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mechanisms of ion intercalation in the “electrolyte — electrode” systems were studied in papers [22–27] based on the lattice model [28–30] and the Blume-Emery-Griffiths model [31]. Computer simulation studies are very important in this field as well [9,32–34]. In particular, in Refs. [3,33] thermodynamic and structural properties of Li_xTiO_2 were investigated using a cluster expansion method based on calculation of pseudopotential energy, which correctly predicts phase behavior of Li intercalation into TiO_2 and occupation of sites. The cluster expansion allows to carry out Monte Carlo calculations of thermodynamics. This makes it possible to determine a configuration of lithium and its chemical potential as a function of lithium concentration at temperature 300 K. For Li_xTiO_2 at $\frac{1}{2} < x < 1$ a two-phase region was obtained, which is consistent with the experiments on diffraction. In Ref. [34] microstructures on surfaces of graphite particles detected in carbon anodes were investigated by means of high-resolution electron microscopy. The surfaces consist of structures built on similarly to carbon nanotubes. Mechanism of formation of these nanostructures was investigated using the method of molecular dynamics based on the Tersoff potential. Electrochemical measurements showed that carbon anodes composed of these structures provide high performance of the battery with a high discharge capacity and low irreversible capacity.

In Ref. [28] intercalation of ions into the base material is studied using the distortion lattice gas model. It was shown that the effective potential of ions arises from the host distortion induced by intercalation. This interaction induces a distinct peak at the flow-concentration diagram. Effective potential can be a negative in a certain region. It means that there is a region with attraction, which is the limit for increasing the distortion effect. Under these conditions intercalants condense around the deformed domains of the host. This consists with the experiments on $\text{Li}_x\text{Mn}_2\text{O}_4$ in which a similar formation of a drop was observed. It turns out that the effect of permselection plays an important role in the electrochemical intercalation. It is important to note the results of paper [31] in which the pseudospin-electron model based on the Blum-Emery-Griffiths one is used to describe the phase transitions and phase separations in the intercalated crystals. It is shown that due to the nature of one-site electron-electron and electron-pseudospin interactions the partition function of this model can be represented as a product of the partition functions of independent pseudospin (with two shifted parameters) and electron subsystems. The phase diagrams of the model, diagrams of the phase separations and concentrations of the intercalated particles depending on their chemical potential were built exactly for zero temperature and in the mean-field approximation for nonzero temperature. It was shown that in some range of values of the chemical potential, direct interaction between intercalated particles and the basic layer of electrons leads to a separation in phases with different concentration of particles and electrons.

The theoretical and experimental studies of chemical diffusion coefficient for lithium ions in intercalation processes into various electrode materials are actively carried out [35–40]. A complicated dependence of chemical diffusion coefficient on a degree of electrochemical intercalation and on alteration of structure of cathode material is analyzed as well. In particular, in Ref. [35] based on a detailed analysis of experimental investigations for various materials an important conclusion was drawn: the structure of intercalated material has the main influence on the chemical diffusion coefficient. Consequently, it is important to take into account to some extent the altering of microstructure of cathode material, in particular, via its polarization properties.

In the present paper we propose a statistical theory to description of electro-diffusion processes in “electrolyte — electrode” system while taking electromagnetic processes into account by means of the D. Zubarev nonequilibrium statistical operator (NSO) method [41,42]. In section 2 we formulate the model and its Hamiltonian. In the third section, using the Zubarev NSO method [41,42] we obtain the nonequilibrium statistical operator for the “electrolyte — electrode” system as a function of corresponding parameters of a reduced description (observables). We receive the generalized transport equations of the Nernst-Planck type for ions and electrons for description of electro-diffusion processes of intercalation. In section 4 the set of equations for ion and electron flows in the “electrolyte — electrode” system is obtained. In these equations mechanisms of transport are described by the gen-

eralized diffusion coefficients which are calculated in the fifth section in Gaussian approximation for time dependence via the zero and the second moments of time correlation function.

2. Hamiltonian of the system

Physical processes in batteries during charging and discharging can be divided into transitional (with nonstationary flows of ions and electrons) and stationary (with stationary flows of ions and electrons) ones. The driving forces of these processes are differences in potentials of electric fields of an electrolyte and an electrode. When we deal with the transitional processes (including charging or discharging) the potentials of electric fields are not stationary and according to Maxwell's equations for electromagnetic fields in each subsystem vector potential acts on each charged particle and determines the nonequilibrium magnetic field. Transitional processes are fast processes of charge transport between the electrodes which lead to strong polarization in the electrolyte and electrode, namely to the change of dynamic dielectric functions. Obviously, for each transitional process, there is its own characteristic time of charge transport by ions and electrons, in particular, time of ion intercalation/deintercalation into the electrode structure. Intercalation of ions into the electrode structure on the stage of transitional processes modifies strongly a dielectric function of the electrode and electrolyte which apparently, via the relaxation phenomena induce stationary processes of charging and discharging of the battery, time of which is much larger than the time of transitional processes. That is, the stationary processes of charge transport are formed by strongly polarization subsystems of the electrolyte and electrode on the stage of transition processes.

We consider the electrolyte – electrode system, when electrolyte is presented as a classical subsystem of interacting ions, electrons and molecules, whereas the electrode is presented as a quantum subsystem, in which ions can intercalate from solution. We consider ion model with the Hamiltonian on the stage of transitional processes represented as

$$H = H^f + H^{int} + H^s. \quad (1)$$

Here,

$$H^f = H_i + \sum_{\alpha} \sum_{j=1}^{N_{\alpha}} Z_{\alpha} e \varphi_f(\mathbf{r}_j; t)$$

is the Hamiltonian of the electrolyte subsystem, positively and negatively charged ions of which are considered on the classical level of interactions in the solution with a dielectric function,

$$H_i = \sum_{\alpha} \sum_{j=1}^{N_{\alpha}} \frac{1}{2m_{\alpha}} \left(\mathbf{p}_j - \frac{Z_{\alpha} e}{c} \mathbf{A}_f(\mathbf{r}_j; t) \right)^2 + \sum_{\alpha\beta} \sum_{j \neq k=1}^{N_{\alpha} N_{\beta}} V_{\alpha\beta}(\mathbf{r}_j, \mathbf{r}_k) \quad (2)$$

is the Hamiltonian of ions, \mathbf{p}_j is the momentum of j th ion of species α having mass m_{α} ; $V_{\alpha\beta}(\mathbf{r}_j, \mathbf{r}_k) = \frac{Z_{\alpha} Z_{\beta} e^2}{r_{jk}}$ is the Coloumb interaction between ions of valences Z_{α} and Z_{β} , e is the electron charge and r_{jk} is the distance between ions.

H^{int} is the Hamiltonian describing interaction of ions and electrons of electrolyte with the surface of electrode. It should describe a polarization, an adsorption and other surface properties. This is important for the formation of “electrolyte – electrode” interface at the negatively charged electrode, which affects the cyclic charge/discharge processes and the life time of battery [8]. The potential can be modeled on the both classical and quantum levels depending on the model.

H^s is the Hamiltonian describing the interaction of the intercalated ions and electrons with the electrode structure (it may be an insulator with the layered structure or other porous one):

$$H^s = H_i^s + H_e + V_{ei}.$$

Here,

$$H_i^s = \frac{\hbar^2}{2m_\alpha} \sum_{j=1}^{N_\alpha} \left(\nabla_j - \frac{Z_\alpha e}{c} \mathbf{A}_s(\mathbf{r}_j; t) \right)^2 + V_{ii} + V_{is} + \sum_{\alpha} \sum_{j=1}^{N_\alpha} Z_\alpha e \varphi_s(\mathbf{r}_j; t) \quad (3)$$

is the Hamiltonian of ions intercalated in the structure of the electrode with the model interaction potential V_{ii} ; V_{is} is potential of interaction of ions with the structure of the electrode and V_{ie} is the model interaction potential of intercalated ions and electrons described by the Hamiltonian:

$$H_e = \frac{\hbar^2}{2m_e} \sum_{j=1}^{N_e} \left(\nabla_j - \frac{e}{c} \mathbf{A}_s(\mathbf{r}_j; t) \right)^2 + V_{ee} + V_{es} + \sum_{j=1}^{N_e} e \varphi_s(\mathbf{r}_j; t) \quad (4)$$

which is the complete Hamiltonian of the electron subsystem in the structure of the electrode. $\mathbf{A}_s(\mathbf{r}_j; t)$, $\varphi_s(\mathbf{r}_j; t)$ are vector and scalar potential of the electromagnetic field acting on electrons and ions intercalated in the matrix of the electrode with dielectric function ε_f . V_{es} is the potential of interaction of electrons with the structure of electrode. $\mathbf{A}_f(\mathbf{r}_j; t)$, $\mathbf{A}_s(\mathbf{r}_j; t)$ and $\varphi_f(\mathbf{r}_j; t)$, $\varphi_s(\mathbf{r}_j; t)$ are the vector and the scalar potentials of the electromagnetic field, which during the charging/discharging of batteries are the driving forces of transport processes of ions in the electrolyte and intercalated ions and electrons in the electrode. They form the transitional processes that significantly change the polarization properties of both electrolyte and electrode, which in turn lead to a redistribution of charge, certain orientation of the polarized solvent molecules and the emergence of a stationary flows of ions and electrons in the processes of charging or discharging of the battery.

3. Nonequilibrium statistical operator of the “electrolyte — electrode” system

The nonequilibrium state of the “electrolyte — electrode” system can be described by the reduced set of observed variables:

$$n_\alpha^f(\mathbf{r}, t) = \langle \hat{n}_\alpha^f(\mathbf{r}) \rangle^t, \quad (5)$$

which are the average values of densities of ions in the electrolyte subsystem. Here, $\hat{n}_\alpha(\mathbf{r}_f) = \sum_{j=1}^{N_\alpha} \delta(\mathbf{r}_f - \mathbf{r}_j)$ are the microscopic densities of ions of species α in the electrolyte with the dielectric function ε_f .

$$n_\alpha(\mathbf{r}_s, t) = \langle \hat{n}_\alpha(\mathbf{r}_s) \rangle^t, \quad n_e(\mathbf{r}_s, t) = \langle \hat{n}_e(\mathbf{r}_s) \rangle^t, \quad (6)$$

are the nonequilibrium average densities of intercalated ions and electrons in the electrode structure with the dielectric function ε_s . Here, the quantum operators of density of ions $\hat{n}_\alpha(\mathbf{r}_s) = \hat{\Psi}_\alpha^+(\mathbf{r}_s) \hat{\Psi}_\alpha(\mathbf{r}_s)$ and electrons $\hat{n}_e(\mathbf{r}_s) = \hat{\Psi}_e^+(\mathbf{r}_s) \hat{\Psi}_e(\mathbf{r}_s)$ are built on the creation $\hat{\Psi}_\alpha^+(\mathbf{r}_s)$, $\hat{\Psi}_e^+(\mathbf{r}_s)$ and annihilation $\hat{\Psi}_\alpha(\mathbf{r}_s)$, $\hat{\Psi}_e(\mathbf{r}_s)$ operators. Index “f” denotes the electrolyte subsystem, and “s” corresponds to electrode. In Eqs. (5) and (6) the nonequilibrium averages $\langle \dots \rangle^t = \text{Sp} \dots \rho(t)$ and are calculated using the nonequilibrium statistical operator $\rho(t)$ for particles of the “electrolyte — electrode” system. To find it we use the Zubarev NSO method [41,42], where nonequilibrium statistical operator of the system is obtained as a solution of the Liouville equation $\frac{\partial}{\partial t} \rho(t) + iL(t)\rho(t) = -\varepsilon(\rho(t) - \rho_q(t))$ with a source $\varepsilon(\rho(t) - \rho_q(t))$. The latter describes the relaxation of the distribution $\rho(t)$ to $\rho_q(t)$, which is determined from the extremum of the information entropy at fixed values of the parameters of reduced description

and saving the normalization condition. In general form, the solution of Liouville equation can be presented as follows:

$$\rho(t) = \rho_q(t) - \int_{-\infty}^t e^{\varepsilon(t'-t)} T(t, t') (1 - P_q(t')) iL \rho_q(t') dt', \quad (7)$$

where iL is the Liouville operator corresponding to the Hamiltonian of the model (1).

$$T(t, t') = \exp \left(- \int_{t'}^t (1 - P_q(t'')) iL dt'' \right) \quad (8)$$

is the generalized evolution operator containing the Kawasaki-Gunton projection $P_q(t')$ whose structure depends on the structure of quasiequilibrium statistical operator $\rho_q(t)$ for the selected set of reduced description parameters. In our case, $\rho_q(t)$ calculated from the extremum of the information entropy at fixed values of the observed variables (5) and (6) and the normalization condition $\int d\Gamma \rho_q(t) = 1$ can be presented in the following form

$$\rho_q(t) = \exp \left\{ - \Phi(t) - \beta \left(H' - \sum_l \sum_{\alpha} \int d\mathbf{r}_l (\mu_{\alpha}(\mathbf{r}_l; t) + Z_{\alpha} e \varphi(\mathbf{r}_l; t)) \hat{n}_{\alpha}(\mathbf{r}_l) - \int d\mathbf{r}_s (\mu_e(\mathbf{r}_s; t) - e \varphi(\mathbf{r}_s; t)) \hat{n}_e(\mathbf{r}_s) \right) \right\}, \quad (9)$$

where

$$\Phi(t) = \ln \int d\Gamma \exp \left\{ \beta \left(H' - \sum_l \sum_{\alpha} \int d\mathbf{r}_l (\mu_{\alpha}(\mathbf{r}_l; t) + Z_{\alpha} e \varphi(\mathbf{r}_l; t)) \hat{n}_{\alpha}^l(\mathbf{r}_l) - \int d\mathbf{r}_s (\mu_e(\mathbf{r}_s; t) - e \varphi(\mathbf{r}_s; t)) \hat{n}_e^l(\mathbf{r}_s) \right) \right\} \quad (10)$$

is the Massieu-Planck functional [41,42] ($l = f; s$). In these relations,

$$H' = \sum_{\alpha} \sum_{j=1}^{N_{\alpha}} \frac{1}{2m_{\alpha}} p_j^2 + \frac{\hbar^2}{2m_{\alpha}} \sum_{j=1}^{N_{\alpha}} (\nabla_j)^2 + \sum_{\alpha\beta} \sum_{j \neq k=1}^{N_{\alpha} N_{\beta}} V_{\alpha\beta}(\mathbf{r}_j, \mathbf{r}_k) + V_{ii} + V_{ie} + \frac{\hbar^2}{2m_e} \sum_{j=1}^{N_e} (\nabla_j)^2 + V_{ee}. \quad (11)$$

$\mu_{\alpha}(\mathbf{r}_l; t)$ denotes a local nonequilibrium value of the chemical potential of ions of species α , and $\mu_e(\mathbf{r}_s; t)$ is a local nonequilibrium value of the chemical potential of electrons, which are determined from the self-consistency conditions:

$$\langle n_{\alpha}(\mathbf{r}_l) \rangle^t = \langle \hat{n}_{\alpha}(\mathbf{r}_l) \rangle_q^t, \quad \langle n_e(\mathbf{r}_s) \rangle^t = \langle \hat{n}_e(\mathbf{r}_s) \rangle_q^t. \quad (12)$$

Quasiequilibrium statistical operator $\rho_q(t)$ describes the dynamic equilibrium of charge distribution in the “electrolyte – electrode” system.

Further, we consider the nonequilibrium transport processes of ions and electrons in the system when the deviations $\delta\mu_{\alpha}(\mathbf{r}_l; t) = \mu_{\alpha}(\mathbf{r}_l; t) - \mu_{\alpha}$, $\delta\mu_e(\mathbf{r}_s; t) = \mu_e(\mathbf{r}_s; t) - \mu_e$ are small (here μ_{α} , μ_e are the equilibrium values of chemical potential of ions of species α and electrons in respective subsystems).

Then, expanding the quasiequilibrium statistical operator (9) in a series in deviations mentioned above and restricting ourselves by the linear approximation we obtain:

$$\rho_q(t) = \left(1 - \sum_l \sum_\alpha \int d\mathbf{r}_l \delta\mu_\alpha(\mathbf{r}_l; t) \hat{n}_\alpha(\mathbf{r}_l) - \int d\mathbf{r}_s \delta\mu_e(\mathbf{r}_s; t) \hat{n}_e^l(\mathbf{r}_s) \right) \rho_\varphi(t), \quad (13)$$

where

$$\rho_\varphi(t) = \exp \left\{ -\Phi_\varphi(t) - \beta \left(H' - \sum_\alpha \mu_\alpha n_\alpha - \mu_e n_e - \sum_l \sum_\alpha \int d\mathbf{r}_l Z_\alpha e\varphi(\mathbf{r}_l; t) \hat{n}_\alpha(\mathbf{r}_l) + \int d\mathbf{r}_s e\varphi(\mathbf{r}_s; t) \hat{n}_e(\mathbf{r}_s) \right) \right\} \quad (14)$$

is a new quasiequilibrium statistical operator and

$$\hat{n}_e(\mathbf{r}_s; \tau) = \int_0^1 d\tau \rho_\varphi^\tau(t) \hat{n}_e(\mathbf{r}_s) \rho_\varphi^{-\tau}(t),$$

$$\hat{n}_\alpha(\mathbf{r}_l; \tau) = \int_0^1 d\tau \rho_\varphi^\tau(t) \hat{n}_\alpha(\mathbf{r}_l) \rho_\varphi^{-\tau}(t)$$

are quantum operators. Determining the parameters $\delta\mu_\alpha(\mathbf{r}_l; t), \delta\mu_e(\mathbf{r}_s; t)$ in (13) from the self-consistency conditions (12) we obtain the following expression for the quasiequilibrium statistical operator:

$$\rho_q(t) = \left(1 + \sum_{l,l'} \sum_{\alpha\gamma} \int d\mathbf{r}_l \int d\mathbf{r}_{l'} \delta n_\gamma(\mathbf{r}_{l'}; t) [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l'}, \mathbf{r}_l; t)]_{\gamma\alpha} \hat{n}_\alpha(\mathbf{r}_l) + \int d\mathbf{r}_s \int d\mathbf{r}_{s'} \delta \bar{n}_e(\mathbf{r}_{s'}; t) [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s'}, \mathbf{r}_s; t)]_{ee} \bar{n}_e(\mathbf{r}_s; \tau) \right) \rho_\varphi(t), \quad (15)$$

where $\delta n_\gamma(\mathbf{r}_{l'}; t) = \langle \hat{n}_\gamma(\mathbf{r}_{l'}) \rangle^t - \langle \hat{n}_\gamma(\mathbf{r}_{l'}) \rangle_\varphi^t$, $\delta \bar{n}_e(\mathbf{r}_{s'}; t) = \langle \bar{n}_e(\mathbf{r}_{s'}) \rangle^t - \langle \bar{n}_e(\mathbf{r}_{s'}) \rangle_\varphi^t$ and the average values $\langle \hat{n}_\gamma(\mathbf{r}_l) \rangle_\varphi^t, \langle \bar{n}_e(\mathbf{r}_s) \rangle_\varphi^t$ are calculated using the quasiequilibrium statistical operator (9). $[\tilde{\Phi}_d^{-1}(\mathbf{r}_{l'}, \mathbf{r}_l; t)]_{\gamma\alpha}, [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s'}, \mathbf{r}_s; t)]_{ee}$ elements of the matrix inverse to the matrix $\tilde{\Phi}_d(\mathbf{r}_{l'}, \mathbf{r}_l; t)$ whose elements are Kubo-like quasiequilibrium correlation functions “density-density”

$$\Phi_{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t) = \langle \hat{n}_\alpha(\mathbf{r}_l) \hat{n}_\gamma(\mathbf{r}_{l'}; \tau) \rangle_\varphi^t, \quad (16)$$

$$\Phi_{ee}(\mathbf{r}_s, \mathbf{r}_{s'}; t) = \langle \bar{n}_e(\mathbf{r}_s) \bar{n}_e(\mathbf{r}_{s'}; \tau) \rangle_\varphi^t. \quad (17)$$

In Eqs. (16), (17) a new renormalized density operator for the electronic subsystem appears

$$\bar{n}_e(\mathbf{r}_s) = \hat{n}_e(\mathbf{r}_s) - \sum_{l,l'} \sum_{\alpha\gamma} \int d\mathbf{r}_l \int d\mathbf{r}_{l'} \Phi_{e\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}; t) [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l'}, \mathbf{r}_l; t)]_{\gamma\alpha} \hat{n}_\alpha(\mathbf{r}_l).$$

It arises in a result of the exclusion of parameters $\delta\mu_\alpha(\mathbf{r}_l; t), \delta\mu_e(\mathbf{r}_s; t)$ in $\rho_q(t)$ using the corresponding self-consistency conditions (12). Here,

$$\Phi_{e\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}; t) = \langle \hat{n}_e(\mathbf{r}_s) \hat{n}_\gamma(\mathbf{r}_{l'}; \tau) \rangle_\varphi^t, \quad (18)$$

$$\Phi_{ee}(\mathbf{r}_s, \mathbf{r}_{s'}; t) = \langle \hat{n}_e(\mathbf{r}_s) \hat{n}_e(\mathbf{r}_{s'}; \tau) \rangle_\varphi^t, \quad (19)$$

and $[\tilde{\Phi}^{-1}(\mathbf{r}_{l'}, \mathbf{r}_l; t)]_{\gamma\alpha}$ are the elements of the matrix inverse to the matrix $\tilde{\Phi}(\mathbf{r}_{l'}, \mathbf{r}_l; t)$, whose elements are quasiequilibrium correlation functions (16), (18) and (19). It is important to note that $\hat{n}_\gamma(\mathbf{r}_{l'})$ and $\bar{n}_e(\mathbf{r}_{s'})$ are orthogonal in the sense that $\langle \hat{n}_\gamma(\mathbf{r}_{l'}) \bar{n}_e(\mathbf{r}_{s'}) \rangle_\varphi^t = 0$ and, therefore, the matrix $\tilde{\Phi}_d(\mathbf{r}_{l'}, \mathbf{r}_l; t)$ is diagonal. In correlation function $\Phi_{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t)$, if ions of α and γ species are located in the electrolyte solution, the $\hat{n}_\alpha(\mathbf{r}_l)$ and $\hat{n}_\gamma(\mathbf{r}_{l'})$ are classic dynamic variables, if the ions are located in the electrode subsystem then $\hat{n}_\alpha(\mathbf{r}_l)$ and $\hat{n}_\gamma(\mathbf{r}_{l'})$ are quantum density operators. In a similar manner, we also have the correlation functions for the densities of ions located in the electrolyte and electrode. $\Phi_{e\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}; t)$ is the quasiequilibrium correlation function of electrons density in the electrode subsystem and ions density in the electrolyte or electrode.

Substituting (15) into (7) we obtain the following expression for the nonequilibrium statistical operator:

$$\begin{aligned}
\rho(t) = & \rho_q(t) - \int_{-\infty}^t e^{\varepsilon(t'-t)} T_q(t, t') \left[\beta \sum_{l\alpha} \int d\mathbf{r}_l (1 - P(t')) \dot{\hat{n}}_\alpha(\mathbf{r}_l) Z_\alpha e\varphi(\mathbf{r}_l; t') \right. \\
& - \beta \int d\mathbf{r}_s (1 - P(t')) \dot{\hat{n}}_e(\mathbf{r}_s) e\varphi(\mathbf{r}_s; t') \left. \right] \rho_\varphi(t') dt' \\
& - \int_{-\infty}^t e^{\varepsilon(t'-t)} T_q(t, t') \left[\sum_{l,l'} \sum_{\alpha\gamma} \int d\mathbf{r}_l \int d\mathbf{r}_{l'} \delta n_\gamma(\mathbf{r}_{l'}; t') [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l'}, \mathbf{r}_l; t')]_{\gamma\alpha} (1 - P(t')) \dot{\hat{n}}_\alpha(\mathbf{r}_l) \right. \\
& + \left. \int d\mathbf{r}_s \int d\mathbf{r}_{s'} \delta \bar{n}_e(\mathbf{r}_{s'}; t') [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s'}, \mathbf{r}_s; t')]_{ee} (1 - P(t')) \dot{\hat{n}}_e(\mathbf{r}_s; \tau) \right] \rho_\varphi(t') dt' \\
& - \int_{-\infty}^t e^{\varepsilon(t'-t)} T_q(t, t') \left[\beta \sum_{l,l',l''} \sum_{\alpha\gamma\alpha'} \int d\mathbf{r}_l \int d\mathbf{r}_{l'} \int d\mathbf{r}_{l''} Z_\alpha e\varphi(\mathbf{r}_l; t') \right. \\
& \times \delta n_\gamma(\mathbf{r}_{l''}; t') [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l''}, \mathbf{r}_{l'}; t')]_{\gamma\alpha'} [(1 - P(t')) \dot{\hat{n}}_\alpha(\mathbf{r}_l)] \hat{n}_{\alpha'}(\mathbf{r}_{l'}) \\
& + \beta \sum_l \sum_\alpha \int d\mathbf{r}_l \int d\mathbf{r}_s \int d\mathbf{r}_{s'} Z_\alpha e\varphi(\mathbf{r}_l; t') \delta \bar{n}_e(\mathbf{r}_{s'}; t') [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s'}, \mathbf{r}_s; t')]_{ee} ((1 - P(t')) \dot{\hat{n}}_\alpha(\mathbf{r}_l)) \bar{n}_e(\mathbf{r}_s; \tau) \\
& - \beta \sum_{l,l'} \sum_{\alpha\gamma} \int d\mathbf{r}_l \int d\mathbf{r}_{l'} \int d\mathbf{r}_s e\varphi(\mathbf{r}_s; t') \delta n_\gamma(\mathbf{r}_{l'}; t') [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l'}, \mathbf{r}_l; t')]_{\gamma\alpha} [(1 - P(t')) \dot{\hat{n}}_e(\mathbf{r}_l)] \hat{n}_\alpha(\mathbf{r}_l) \\
& \left. - \beta \int d\mathbf{r}_s \int d\mathbf{r}_{s'} \int d\mathbf{r}_{s''} e\varphi(\mathbf{r}_s; t') \delta \bar{n}_e(\mathbf{r}_{s''}; t') [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s''}, \mathbf{r}_{s'}; t')]_{ee} [(1 - P(t')) \dot{\hat{n}}_e(\mathbf{r}_s)] \bar{n}_e(\mathbf{r}_{s'}; \tau) \right] \rho_\varphi(t') dt'.
\end{aligned} \tag{20}$$

Using the NSO (20) we can build the transport equations for the nonequilibrium average values $\langle \hat{n}_\alpha(\mathbf{r}_l) \rangle^t$, $\langle \bar{n}_e(\mathbf{r}_s) \rangle^t$. Here, $P(t)$ is the generalized Mori projection operator which acts on dynamic variables (quantum operators) and has the following structure:

$$P(t)\hat{A} = \langle \hat{A} \rangle_q^t + \sum_{l,\alpha} \int d\mathbf{r}_l \frac{\delta \langle \hat{A} \rangle_q^t}{\delta \langle \hat{n}_\alpha(\mathbf{r}_l) \rangle^t} (\hat{n}_\alpha(\mathbf{r}_l) - \langle \hat{n}_\alpha(\mathbf{r}_l) \rangle^t) + \int d\mathbf{r}_s \frac{\delta \langle \hat{A} \rangle_q^t}{\delta \langle \hat{n}_e(\mathbf{r}_s) \rangle^t} (\hat{n}_e(\mathbf{r}_s) - \langle \hat{n}_e(\mathbf{r}_s) \rangle^t). \tag{21}$$

It possesses the properties $P(t)(1 - P(t)) = 0$, $P(t)\hat{n}_\alpha(\mathbf{r}_l) = \hat{n}_\alpha(\mathbf{r}_l)$, $P(t)\hat{n}_e(\mathbf{r}_s) = \hat{n}_e(\mathbf{r}_s)$ and is connected with the Kawasaki-Gunton projection operator by the relation

$$P_q(t)\hat{A}\rho_q(t) = \int_0^1 d\tau \rho_q^\tau(t) P(t)\hat{A}\rho_q^{1-\tau}(t)$$

when \hat{A} are quantum operators, and by the relation $P_q(t)\hat{A}\rho_q(t) = \rho_q(t)P_q(t)\hat{A}$, when \hat{A} are classical dynamical variables. In the case of quasiequilibrium statistical operator (15), $P_q(t)$ has the form

$$P(t)\rho' = \left(\rho_q(t) - \sum_{l,\alpha} \int d\mathbf{r}_l \frac{\delta\rho_q(t)}{\delta\langle\hat{n}_\alpha(\mathbf{r}_l)\rangle^t} \langle\hat{n}_\alpha(\mathbf{r}_l)\rangle^t - \int d\mathbf{r}_s \frac{\delta\rho_q(t)}{\delta\langle\hat{n}_e(\mathbf{r}_s)\rangle^t} \langle\hat{n}_e(\mathbf{r}_s)\rangle^t \right) \text{Sp}\rho' \sum_{l,\alpha} \int d\mathbf{r}_l \frac{\delta\rho_q(t)}{\delta\langle\hat{n}_\alpha(\mathbf{r}_l)\rangle^t} \text{Sp}(\hat{n}_\alpha(\mathbf{r}_l)\rho') - \int d\mathbf{r}_s \frac{\delta\rho_q(t)}{\delta\langle\hat{n}_e(\mathbf{r}_s)\rangle^t} \text{Sp}(\hat{n}_e(\mathbf{r}_s)\rho').$$

It acts on the statistical operators $P_q(t)\rho(t) = \rho_q(t)$ and possesses the properties $P_q(t)\rho_q(t) = \rho_q(t)$ and $P_q(t)(1 - P_q(t')) = 0$. For description of transport processes of ions in the “electrolyte – electrode” system using nonequilibrium statistical operator (20) we can obtain the generalized transport equation of the Nernst-Planck type:

$$\frac{\partial}{\partial t} \langle\delta\hat{n}_\alpha(\mathbf{r}_l)\rangle^t = \frac{\partial}{\partial \mathbf{r}_l} \left(\mathbf{j}_\alpha^{(1)}(\mathbf{r}_l; t) + \mathbf{j}_\alpha^{(2)}(\mathbf{r}_l; t) + \mathbf{j}_\alpha^{(3)}(\mathbf{r}_l; t) \right), \quad (22)$$

where the ion flows have the following structure:

$$\begin{aligned} \mathbf{j}_\alpha^{(1)}(\mathbf{r}_l; t) = & \sum_{l',\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta D_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t') dt' \\ & - \int d\mathbf{r}_{s'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta D_{jj}^{\alpha e}(\mathbf{r}_l, \mathbf{r}_{s'}; t, t') \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t') dt', \end{aligned} \quad (23)$$

$$\begin{aligned} \mathbf{j}_\alpha^{(2)}(\mathbf{r}_l; t) = & \sum_{l',\gamma} \int d\mathbf{r}_{l'} \sum_{l'',\alpha'} \int_{-\infty}^t e^{\varepsilon(t'-t)} D_{jj}^{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l''}; t, t') \frac{\partial}{\partial \mathbf{r}_{l''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l' l''}; t')]_{\alpha'\gamma} \delta n_\gamma(\mathbf{r}_{l'}; t') dt' \\ & + \int d\mathbf{r}_{s'} \int_{-\infty}^t e^{\varepsilon(t'-t)} D_{jj}^{\alpha e}(\mathbf{r}_l, \mathbf{r}_{s''}; t, t') \frac{\partial}{\partial \mathbf{r}_{s''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s' s''}; t')]_{ee} \delta \bar{n}_e(\mathbf{r}_{s'}; t') dt, \end{aligned} \quad (24)$$

$$\begin{aligned} \mathbf{j}_\alpha^{(3)}(\mathbf{r}_l; t) = & \sum_{l',\gamma} \sum_{\alpha'\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \bar{D}_{jjn}^{\alpha\alpha'\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \beta \frac{\partial}{\partial \mathbf{r}_{l'}} Z_{\alpha'} e\varphi(\mathbf{r}_{l'}; t') \delta n_\gamma(\mathbf{r}_{l'}; t') dt' \\ & + \sum_{l',\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta \bar{D}_{jjn}^{\alpha\gamma e}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t') \delta \bar{n}_e(\mathbf{r}_{s'}; t') dt' \\ & - \sum_{l',\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta \bar{D}_{jjn}^{\alpha e\gamma}(\mathbf{r}_l, \mathbf{r}_{s'}; t, t') \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t') \delta n_\gamma(\mathbf{r}_{l'}; t') dt' \\ & - \int d\mathbf{r}_{s'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta \bar{D}_{jjn}^{\alpha ee}(\mathbf{r}_l, \mathbf{r}_{s'}; t, t') \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t') \delta \bar{n}_e(\mathbf{r}_{s''}; t') dt'. \end{aligned} \quad (25)$$

Respectively, for the subsystem of electrons in the electrode structure the transport Nernst-Planck type equation is as follows:

$$\frac{\partial}{\partial t} \langle \delta \bar{n}_e(\mathbf{r}_s) \rangle^t = \frac{\partial}{\partial \mathbf{r}_s} \left(\mathbf{j}_e^{(1)}(\mathbf{r}_s; t) + \mathbf{j}_e^{(2)}(\mathbf{r}_s; t) + \mathbf{j}_e^{(3)}(\mathbf{r}_s; t) \right) \quad (26)$$

with the flows of electrons having the form:

$$\begin{aligned} \mathbf{j}_e^{(1)}(\mathbf{r}_s; t) = & \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta D_{jj}^{e\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}; t, t') \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t') dt' \\ & - \int d\mathbf{r}_{s'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s'}; t, t') \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t') dt', \end{aligned} \quad (27)$$

$$\begin{aligned} \mathbf{j}_e^{(2)}(\mathbf{r}_s; t) = & \sum_{l'\gamma} \int d\mathbf{r}_{l'} \sum_{l''\alpha'} \int_{-\infty}^t e^{\varepsilon(t'-t)} D_{jj}^{e\alpha'}(\mathbf{r}_s, \mathbf{r}_{l''}; t, t') \frac{\partial}{\partial \mathbf{r}_{l''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l''}, \mathbf{r}_{l'}; t')]_{\alpha'\gamma} \delta n_\gamma(\mathbf{r}_{l''}; t') dt' \\ & + \int d\mathbf{r}_{s'} \int_{-\infty}^t e^{\varepsilon(t'-t)} D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s''}; t, t') \frac{\partial}{\partial \mathbf{r}_{s''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s''}, \mathbf{r}_{s'}; t')]_{ee} \delta \bar{n}_e(\mathbf{r}_{s''}; t') dt', \end{aligned} \quad (28)$$

$$\begin{aligned} \mathbf{j}_e^{(3)}(\mathbf{r}_s; t) = & \sum_{l'l''} \sum_{\alpha'\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \bar{D}_{jjn}^{e\alpha'\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t') \beta \frac{\partial}{\partial \mathbf{r}_{l'}} Z_{\alpha'} e\varphi(\mathbf{r}_{l'}; t') \delta n_\gamma(\mathbf{r}_{l''}; t') dt' \\ & + \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta \bar{D}_{jjn}^{e\gamma e}(\mathbf{r}_s, \mathbf{r}_{l'}, \mathbf{r}_{s'}; t, t') \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t') \delta \bar{n}_e(\mathbf{r}_{s'}; t') dt' \\ & - \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta \bar{D}_{jjn}^{e\gamma\gamma}(\mathbf{r}_s, \mathbf{r}_{s'}, \mathbf{r}_{l'}; t, t') \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t') \delta n_\gamma(\mathbf{r}_{l'}; t') dt' \\ & - \int d\mathbf{r}_{s'} \int_{-\infty}^t e^{\varepsilon(t'-t)} \beta \bar{D}_{jjn}^{eee}(\mathbf{r}_s, \mathbf{r}_{s'}, \mathbf{r}_{s''}; t, t') \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t') \delta \bar{n}_e(\mathbf{r}_{s''}; t') dt'. \end{aligned} \quad (29)$$

Here,

$$D_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') = \left\langle (1 - P(t')) \hat{\mathbf{j}}_\alpha(\mathbf{r}_l) T_q(t, t') (1 - P(t')) \hat{\mathbf{j}}_\gamma(\mathbf{r}_{l'}) \right\rangle_\varphi^t \quad (30)$$

is the generalized diffusion coefficient of ions as a function of coordinates and time. When $l = f$ and $l' = f'$, we have diffusion coefficient in electrolyte solution. $\hat{\mathbf{j}}_\alpha(\mathbf{r}_f) = \frac{1}{m_\alpha} \sum_{j=1}^{N_\alpha} \mathbf{p}_j \delta(\mathbf{r}_f - \mathbf{r}_j)$ is the current density of ions of species α in the electrolyte solution. When $l = f$ and $l' = s'$, we have a cross-diffusion coefficient for ions in the electrolyte solution and electrode. In this case, $\hat{\mathbf{j}}_\alpha(\mathbf{r}_s) = \frac{\hbar}{im_\alpha} (\hat{\Psi}_\alpha^+(\mathbf{r}_s) \nabla_s \hat{\Psi}_\alpha(\mathbf{r}_s) - \nabla_s \hat{\Psi}_\alpha^+(\mathbf{r}_s) \hat{\Psi}_\alpha(\mathbf{r}_s))$ is the operator of current density of ions in the electrode structure. When $l = s$ and $l' = s'$, we have the generalized quantum diffusion coefficient for ions in

the electrode subsystem.

$$D_{jj}^{\alpha e}(\mathbf{r}_l, \mathbf{r}_{s'}; t, t') = \left\langle (1 - P(t')) \hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l) T_q(t, t') \int_0^1 d\tau \rho_{\varphi}^{\tau}(t) (1 - P(t')) \hat{\mathbf{j}}_e(\mathbf{r}_{s'}) \rho_{\varphi}^{-\tau}(t) \right\rangle_{\varphi}^{t'} \quad (31)$$

defines a generalized coefficient of ion-electron diffusion, herewith, ion can be in the electrolyte subsystem or in the electrode one. Here, $\hat{\mathbf{j}}_e(\mathbf{r}_s) = \frac{\hbar}{ime} (\hat{\Psi}_e^+(\mathbf{r}_s) \nabla_s \hat{\Psi}_e(\mathbf{r}_s) - \nabla_s \hat{\Psi}_e^+(\mathbf{r}_s) \hat{\Psi}_e(\mathbf{r}_s))$ is the operator of current density of ions in the electrode structure. Thus, $D_{jj}^{\alpha e}(\mathbf{r}_f, \mathbf{r}_{s'}; t, t')$ represents a correlation between the currents of electrons and ions in the electrolyte and the electrode, i.e., the interfacial diffusion coefficient. Obviously, it plays an important role in the intercalation of ions into the structure of the electrode. In a similar way, $D_{jj}^{\alpha e}(\mathbf{r}_s, \mathbf{r}_{s'}; t, t')$ represents a correlation between the currents of ions and electrons in the electrode. This is the quantum diffusion coefficient which plays an important role in the processes of ions localization in the electrode structure. These processes are also affected by the quantum diffusion coefficient of electrons in the electrode structure $D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s'}; t, t')$. In fact, we have a matrix of the generalized diffusion coefficients of ions and electrons for the “electrolyte — electrode” system:

$$\mathfrak{D}(\mathbf{r}_l, \mathbf{r}_{l'}) = \begin{vmatrix} D_{jj}^{++}(\mathbf{r}_f, \mathbf{r}_{f'}) & D_{jj}^{+-}(\mathbf{r}_f, \mathbf{r}_{f'}) & D_{jj}^{++}(\mathbf{r}_f, \mathbf{r}_{s'}) & D_{jj}^{+e}(\mathbf{r}_f, \mathbf{r}_{s'}) \\ D_{jj}^{-+}(\mathbf{r}_f, \mathbf{r}_{f'}) & D_{jj}^{--}(\mathbf{r}_f, \mathbf{r}_{f'}) & D_{jj}^{-+}(\mathbf{r}_f, \mathbf{r}_{s'}) & D_{jj}^{-e}(\mathbf{r}_f, \mathbf{r}_{s'}) \\ D_{jj}^{++}(\mathbf{r}_s, \mathbf{r}_{f'}) & D_{jj}^{+-}(\mathbf{r}_s, \mathbf{r}_{f'}) & D_{jj}^{++}(\mathbf{r}_s, \mathbf{r}_{s'}) & D_{jj}^{+e}(\mathbf{r}_s, \mathbf{r}_{s'}) \\ D_{jj}^{e+}(\mathbf{r}_s, \mathbf{r}_{f'}) & D_{jj}^{e-}(\mathbf{r}_s, \mathbf{r}_{f'}) & D_{jj}^{e+}(\mathbf{r}_s, \mathbf{r}_{s'}) & D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s'}) \end{vmatrix}_t. \quad (32)$$

In the generalized Nernst-Planck equations an important role belongs to transport kernels

$$\begin{aligned} \bar{D}_{jjn}^{\alpha\alpha'\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t') &= \sum_{l''\alpha''} \int d\mathbf{r}_{l''} \left\langle (1 - P(t')) \hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l) T_q(t, t') (1 - P(t')) \hat{\mathbf{j}}_{\alpha'}(\mathbf{r}_{l'}) \hat{n}_{\alpha''}(\mathbf{r}_{l''}; t') \right\rangle_{\varphi}^{t'} \\ &\times [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l''}, \mathbf{r}_{l''}; t')]_{\alpha''\gamma} \end{aligned} \quad (33)$$

Unlike the transport kernels related with the generalized coefficients, they are the correlation functions of the third order and enter into the equations via the second order in the parameters $\varphi(\mathbf{r}_{l'}; t') \delta n_{\gamma}(\mathbf{r}_{l''}; t')$, $\varphi(\mathbf{r}_{l'}; t') \delta \bar{n}_e(\mathbf{r}_{s'}; t')$, $\varphi(\mathbf{r}_{s'}; t') \delta n_{\gamma}(\mathbf{r}_{l'}; t')$, that describe dynamic correlation between the field and the density fluctuations for ions and electrons. When α corresponds to positively charged ions, equation (22) describes the electrodiffusion processes via the generalized diffusion coefficients. At $l = f$ equation describes temporal and spatial changes of densities of positively charged ions $\langle \hat{n}_+(\mathbf{r}_f) \rangle^t$ in electrolyte. At $l = s$ equation describes the change of $\langle \hat{n}_+(\mathbf{r}_s) \rangle^t$ of ions intercalated into electrode structure. The processes in the corresponding subsystems are described by the generalized diffusion coefficients of positively charged ions $D_{jj}^{++}(\mathbf{r}_f, \mathbf{r}_{f'}; t, t')$ and by the generalized mutual diffusion coefficients of positively and negatively charged ions $D_{jj}^{+-}(\mathbf{r}_f, \mathbf{r}_{f'}; t, t')$ in the electrolyte solution. Equations (22) and (26) for the electronic subsystem include mutual “ion-ion” and “ion-electron” diffusion coefficients $D_{jj}^{++}(\mathbf{r}_f, \mathbf{r}_{s'}; t, t')$ and $D_{jj}^{+e}(\mathbf{r}_f, \mathbf{r}_{s'}; t, t')$ which describe the temporal correlation between flows of ions in electrolyte and flows of ions and electrons in electrode structure. $D_{jj}^{++}(\mathbf{r}_s, \mathbf{r}_{s'}; t, t')$, $D_{jj}^{+e}(\mathbf{r}_s, \mathbf{r}_{s'}; t, t')$, $D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s'}; t, t')$ are the quantum “ion-ion”, “ion-electron” and “electron-electron” diffusion coefficients in the electrode structure.

It is important to note that neglecting the time memory effects and spatial heterogeneity (to make transport coefficients constant) in flows (23)–(25) and (27)–(29), together with the Poisson equations for the potentials $\varphi(\mathbf{r}_{l'}; t')$ we obtain the Poisson-Nernst-Planck equation [6,8]. The corresponding components of the flows of ions and electrons in the system of equations (22), (26) are connected with the corresponding gradients:

$$\frac{\partial}{\partial \mathbf{r}_{l'}} Z_{\gamma} e \varphi(\mathbf{r}_{l'}; t'), \quad \frac{\partial}{\partial \mathbf{r}_{s'}} e \varphi(\mathbf{r}_{s'}; t'), \quad \frac{\partial}{\partial \mathbf{r}_{l''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l''}, \mathbf{r}_{l''}; t')]_{\alpha'\gamma}, \quad \frac{\partial}{\partial \mathbf{r}_{s''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s''}, \mathbf{r}_{s''}; t')]_{ee}.$$

Moreover, gradients of the corresponding potentials

$$\begin{aligned}\frac{\partial}{\partial \mathbf{r}_f} \varphi(\mathbf{r}_f; t') &= \mathbf{E}(\mathbf{r}_f; t'), \\ \frac{\partial}{\partial \mathbf{r}_{s'}} \varphi(\mathbf{r}_{s'}; t') &= \mathbf{E}(\mathbf{r}_{s'}; t')\end{aligned}\quad (34)$$

induce electric fields in the respective subsystems with the corresponding tensors of the dielectric functions.

$$\begin{aligned}\mathbf{D}(\mathbf{r}_f; t') &= \int dt' \int d\mathbf{r}_{f''} \bar{\epsilon}(\mathbf{r}_f, \mathbf{r}_{f''}; t', t'') \mathbf{E}(\mathbf{r}_{f''}; t'), \\ \mathbf{D}(\mathbf{r}_{s'}; t') &= \int dt' \int d\mathbf{r}_{s''} \bar{\epsilon}(\mathbf{r}_{s'}, \mathbf{r}_{s''}; t', t'') \mathbf{E}(\mathbf{r}_{s''}; t')\end{aligned}\quad (35)$$

are the vectors of displacement of electric field in the electrolyte and electrode subsystems, which along with the magnetic induction and the intensity of magnetic field satisfy the Maxwell equation:

$$\begin{aligned}\nabla \cdot \mathbf{B}(\mathbf{r}_f, t) &= 0, \\ \nabla \cdot \mathbf{D}(\mathbf{r}_f, t) &= \sum_{\alpha=1}^N Z_{\alpha} e n_{\alpha}(\mathbf{r}_f, t), \\ \nabla \times \mathbf{E}(\mathbf{r}_f, t) &= -\frac{\partial}{\partial t} \mathbf{B}(\mathbf{r}_f, t), \\ \nabla \times \mathbf{H}(\mathbf{r}_f, t) &= \frac{\partial}{\partial t} \mathbf{D}(\mathbf{r}_f, t) + \sum_{\alpha} Z_{\alpha} e \mathbf{j}_{\alpha}(\mathbf{r}_f, t),\end{aligned}\quad (36)$$

where $\mathbf{B}(\mathbf{r}_f, t)$, $\mathbf{E}(\mathbf{r}_f, t)$ and $\mathbf{D}(\mathbf{r}_f, t)$, $\mathbf{H}(\mathbf{r}_f, t)$ are intensity and induction of the electric and magnetic fields in the electrolyte caused by ions of species α with the density $n_{\alpha}(\mathbf{r}_f, t)$ and the corresponding currents of charge $Z_{\alpha} e \mathbf{j}_{\alpha}(\mathbf{r}_f, t)$.

$$\begin{aligned}\nabla \cdot \mathbf{B}(\mathbf{r}_s, t) &= 0, \\ \nabla \cdot \mathbf{D}(\mathbf{r}_s, t) &= \sum_{\alpha=1}^N Z_{\alpha} e n_{\alpha}(\mathbf{r}_s, t) + e n_e(\mathbf{r}_s, t), \\ \nabla \times \mathbf{E}(\mathbf{r}_s, t) &= \frac{\partial}{\partial t} \mathbf{B}(\mathbf{r}_s, t), \\ \nabla \times \mathbf{H}(\mathbf{r}_s, t) &= \frac{\partial}{\partial t} \mathbf{D}(\mathbf{r}_s, t) + \sum_{\alpha} Z_{\alpha} e \mathbf{j}_{\alpha}(\mathbf{r}_s, t) + e \mathbf{j}_e(\mathbf{r}_s, t),\end{aligned}\quad (37)$$

where $\mathbf{B}(\mathbf{r}_s, t)$, $\mathbf{E}(\mathbf{r}_s, t)$ and $\mathbf{D}(\mathbf{r}_s, t)$, $\mathbf{H}(\mathbf{r}_s, t)$, $\mathbf{j}_{\alpha}^s(\mathbf{r}, t)$, $\mathbf{j}_e^s(\mathbf{r}, t)$ are intensity and induction of the electric and magnetic fields in the electrode caused by ions and electrons with the charge densities $Z_{\alpha} e n_{\alpha}(\mathbf{r}_f, t)$ and $e n_e(\mathbf{r}_s, t)$ and the charge currents $Z_{\alpha} e \mathbf{j}_{\alpha}(\mathbf{r}_f, t)$ and $e \mathbf{j}_e(\mathbf{r}_s, t)$. Both systems of equations for the electrolyte and electrode (22), (26), (34), (35) are related by inter-phase partial diffusion coefficients and boundary conditions at the electrolyte-electrode interface:

$$\begin{aligned}\mathbf{n} \cdot (\mathbf{B}_s - \mathbf{B}_f) &= 0, \\ \mathbf{n} \cdot (\mathbf{D}_s - \mathbf{D}_f) &= Q(\mathbf{S}_{\omega}, t), \\ \mathbf{n} \times (\mathbf{E}_s - \mathbf{E}_f) &= 0, \\ \mathbf{n} \times (\mathbf{H}_s - \mathbf{H}_f) &= Q(\mathbf{S}_{\omega}) \boldsymbol{\nu}_s(\mathbf{S}_{\omega}, t),\end{aligned}$$

where $Q(\mathbf{S}_\omega, t)$ is the total surface electric charge at the “electrolyte – electrode” interface which satisfies the conservation law:

$$\frac{\partial}{\partial t} Q(\mathbf{S}_\omega, t) = \mathbf{n} \cdot \mathbf{j}_i(\mathbf{S}_\omega, t), \quad \nu_s(\mathbf{S}_\omega, t) = \nu_f(\mathbf{S}_\omega, t).$$

\mathbf{n} is a unit vector perpendicular to the interface “electrolyte – electrode”. $\mathbf{j}_i(\mathbf{S}_\omega, t)$ is the average current of the surface charge. At the interface “electrolyte – electrode” \mathbf{S}_ω , the condition of continuity is satisfied

$$\frac{\partial}{\partial t} n_\alpha(\mathbf{S}_\omega, t) = \frac{\partial}{\partial t} n_a^f(\mathbf{S}_\omega, t),$$

which leads to the equation describing the complexity of the transport processes in the “electrolyte – electrode” interface area. It requires a detailed analysis and a separate consideration when a certain model is chosen for the Hamiltonian H_{int} (which describes the interaction of ions of electrolyte with the surface of electrode and should take into account polarization, adsorption and other surface properties).

4. Stationary flows of ions and electrons

Regime of stationary ion and electron flows is an important stage of the battery lifetime. For the study of flows of ions and electrons we differentiate them by time and then obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{j}_\alpha^{(1)}(\mathbf{r}_l; t) &= \sum_{l'\gamma} \int d\mathbf{r}_{l'} \beta D_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t) \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t) \\ &\quad - \int d\mathbf{r}_{s'} \beta D_{jj}^{\alpha e}(\mathbf{r}_l, \mathbf{r}_{s'}; t) \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t), \end{aligned} \quad (38)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{j}_\alpha^{(2)}(\mathbf{r}_l; t) &= \sum_{l'\gamma} \int d\mathbf{r}_{l'} \sum_{l''\alpha'} \int d\mathbf{r}_{l''} D_{jj}^{\alpha\alpha'}(\mathbf{r}_l, \mathbf{r}_{l''}; t) \frac{\partial}{\partial \mathbf{r}_{l''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l''}, \mathbf{r}_{l'}; t)]_{\alpha'\gamma} \delta n_\gamma(\mathbf{r}_{l'}; t) \\ &\quad + \int d\mathbf{r}_{s'} \int d\mathbf{r}_{s''} D_{jj}^{\alpha e}(\mathbf{r}_l, \mathbf{r}_{s''}; t) \frac{\partial}{\partial \mathbf{r}_{s''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s''}, \mathbf{r}_{s'}; t)]_{ee} \delta \bar{n}_e(\mathbf{r}_{s'}; t), \end{aligned} \quad (39)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{j}_\alpha^{(3)}(\mathbf{r}_l; t) &= \sum_{l''\gamma} \sum_{\alpha'\gamma} \int d\mathbf{r}_{l'} \int d\mathbf{r}_{l''} \beta \bar{D}_{jjn}^{\alpha\alpha'\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t) \frac{\partial}{\partial \mathbf{r}_{l'}} Z_{\alpha'} e\varphi(\mathbf{r}_{l'}; t) \delta n_\gamma(\mathbf{r}_{l''}; t) \\ &\quad + \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int d\mathbf{r}_{s'} \beta \bar{D}_{jjn}^{\alpha\gamma e}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{s'}; t) \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t) \delta \bar{n}_e(\mathbf{r}_{s'}; t) \\ &\quad - \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int d\mathbf{r}_{s'} \beta \bar{D}_{jjn}^{\alpha e \gamma}(\mathbf{r}_l, \mathbf{r}_{s'}, \mathbf{r}_{l'}; t) \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t) \delta n_\gamma(\mathbf{r}_{l'}; t) \\ &\quad - \int d\mathbf{r}_{s'} \int d\mathbf{r}_{s''} \beta \bar{D}_{jjn}^{\alpha e e}(\mathbf{r}_l, \mathbf{r}_{s'}, \mathbf{r}_{s''}; t) \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t) \delta \bar{n}_e(\mathbf{r}_{s''}; t) \end{aligned} \quad (40)$$

for ions, and

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{j}_e^{(1)}(\mathbf{r}_s; t) &= \sum_{l'\gamma} \int d\mathbf{r}_{l'} \beta D_{jj}^{e\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}; t) \cdot \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t) \\ &\quad - \int d\mathbf{r}_{s'} \beta D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s'}; t) \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t), \end{aligned} \quad (41)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{j}_e^{(2)}(\mathbf{r}_s; t) &= \sum_{l'\gamma} \int d\mathbf{r}_{l'} \sum_{l''\alpha'} \int d\mathbf{r}_{l''} D_{jj}^{e\alpha'}(\mathbf{r}_s, \mathbf{r}_{l''}; t) \frac{\partial}{\partial \mathbf{r}_{l''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{l''}, \mathbf{r}_{l'}; t)]_{\alpha'\gamma} \delta n_\gamma(\mathbf{r}_{l''}; t) \\ &+ \int d\mathbf{r}_{s'} \int d\mathbf{r}_{s''} D_{jj}^{ee}(\mathbf{r}_s, \mathbf{r}_{s''}; t) \frac{\partial}{\partial \mathbf{r}_{s''}} [\tilde{\Phi}_d^{-1}(\mathbf{r}_{s''}, \mathbf{r}_{s'}; t)]_{ee} \delta \bar{n}_e(\mathbf{r}_{s''}; t), \end{aligned} \quad (42)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{j}_e^{(3)}(\mathbf{r}_s; t) &= \sum_{l''} \sum_{\alpha'\gamma} \int d\mathbf{r}_{l'} \int d\mathbf{r}_{l''} \beta \bar{D}_{jjn}^{e\alpha'\gamma}(\mathbf{r}_s, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t) \frac{\partial}{\partial \mathbf{r}_{l''}} Z_{\alpha'} e\varphi(\mathbf{r}_{l''}; t) \delta n_\gamma(\mathbf{r}_{l''}; t) \\ &+ \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int d\mathbf{r}_{s'} \beta \bar{D}_{jjn}^{e\gamma e}(\mathbf{r}_s, \mathbf{r}_{l'}, \mathbf{r}_{s'}; t) \frac{\partial}{\partial \mathbf{r}_{l'}} Z_\gamma e\varphi(\mathbf{r}_{l'}; t) \delta \bar{n}_e(\mathbf{r}_{s'}; t) \\ &- \sum_{l'\gamma} \int d\mathbf{r}_{l'} \int d\mathbf{r}_{s'} \beta \bar{D}_{jjn}^{ee\gamma}(\mathbf{r}_s, \mathbf{r}_{s'}, \mathbf{r}_{l'}; t) \frac{\partial}{\partial \mathbf{r}_{s'}} e\varphi(\mathbf{r}_{s'}; t) \delta n_\gamma(\mathbf{r}_{l'}; t) \\ &- \int d\mathbf{r}_{s'} \int d\mathbf{r}_{s''} \beta \bar{D}_{jjn}^{eee}(\mathbf{r}_s, \mathbf{r}_{s'}, \mathbf{r}_{s''}; t) \frac{\partial}{\partial \mathbf{r}_{s''}} e\varphi(\mathbf{r}_{s''}; t) \delta \bar{n}_e(\mathbf{r}_{s''}; t) \end{aligned} \quad (43)$$

for electrons. Therefore, transport equations (22), (26) can be rewritten down as follows:

$$\frac{\partial^2}{\partial t^2} \langle \delta \hat{n}_\alpha(\mathbf{r}_l) \rangle^t = \frac{\partial}{\partial t} \frac{\partial}{\partial \mathbf{r}_l} \cdot \left(\mathbf{j}_\alpha^{(1)}(\mathbf{r}_l; t) + \mathbf{j}_\alpha^{(2)}(\mathbf{r}_l; t) + \mathbf{j}_\alpha^{(3)}(\mathbf{r}_l; t) \right) \quad (44)$$

$$\frac{\partial^2}{\partial t^2} \langle \delta \bar{n}_e(\mathbf{r}_s) \rangle^t = \frac{\partial}{\partial t} \frac{\partial}{\partial \mathbf{r}_s} \cdot \left(\mathbf{j}_e^{(1)}(\mathbf{r}_s; t) + \mathbf{j}_e^{(2)}(\mathbf{r}_s; t) + \mathbf{j}_e^{(3)}(\mathbf{r}_s; t) \right). \quad (45)$$

Stationarity of ion and electron flows in the system means that $\frac{\partial}{\partial t} Z_\alpha e(\mathbf{j}_\alpha^{(1)}(\mathbf{r}_l; t) + \mathbf{j}_\alpha^{(2)}(\mathbf{r}_l; t) + \mathbf{j}_\alpha^{(3)}(\mathbf{r}_l; t)) = 0$, $\frac{\partial}{\partial t} e(\mathbf{j}_e^{(1)}(\mathbf{r}_s; t) + \mathbf{j}_e^{(2)}(\mathbf{r}_s; t) + \mathbf{j}_e^{(3)}(\mathbf{r}_s; t)) = 0$. As a result, we obtain a set of equations for the stationary average values of number densities of ions and electrons and the electric field potentials in different subsystems when mechanisms of transport of ions and electrons are described by the stationary values of generalized diffusion coefficients and transport kernels (33).

5. Generalized diffusion coefficients

Since generalized diffusion coefficients (32) and transport kernels (33) can not be calculated exactly, Lorentz or Gaussian approximations of time dependence are frequently used. Expanding evolution operator (8) in $\int_{t'}^t (1 - P_q(t'')) i L dt''$, and calculating the corresponding moments, time correlation function (30) can be presented as follows:

$$D_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') = D_{0jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') e^{-\lambda_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')} (1 + B_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')), \quad (46)$$

where the zero moment

$$D_{0jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') = \left\langle (1 - P(t)) \hat{\mathbf{j}}_\alpha(\mathbf{r}_l) (1 - P(t')) \hat{\mathbf{j}}_e(\mathbf{r}_{s'}) \right\rangle_\varphi^{t'} \quad (47)$$

is a diffusion coefficient of ions in quasiequilibrium state described by distribution (14). In (46)

$$\lambda_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') = \frac{\left\langle (1 - P(t)) \hat{\mathbf{j}}_\alpha(\mathbf{r}_l) \left(\int_{t'}^t (1 - P_q(t'')) i L dt'' \right)^2 (1 - P(t')) \hat{\mathbf{j}}_e(\mathbf{r}_{s'}) \right\rangle_\varphi^{t'}}{\left\langle (1 - P(t)) \hat{\mathbf{j}}_\alpha(\mathbf{r}_l) (1 - P(t')) \hat{\mathbf{j}}_e(\mathbf{r}_{s'}) \right\rangle_\varphi^{t'}} \quad (48)$$

is a normalized second moment. $B_{jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t')$ is a function including higher moments of the correlation function “current-current”. Here we took into account the structure of statistical operator (14) and the action $P(t)\hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l)$. Taking this into consideration we can calculate the zero moment at $l = f, l' = f'$:

$$\begin{aligned} D_{0jj}^{\alpha\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}; t, t') &= \langle \hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l) \hat{\mathbf{j}}_{\epsilon}(\mathbf{r}_{s'}) \rangle_{\varphi}^{t'} \\ &= \left\langle \sum_{j=1}^{N_{\alpha}} \frac{\mathbf{p}_j}{m_{\alpha}} \cdot \frac{\mathbf{p}_j}{m_{\alpha}} \delta(\mathbf{r}_f - \mathbf{r}_j) \right\rangle_{\varphi}^{t'} \delta_{\alpha\gamma} \delta(\mathbf{r}_f - \mathbf{r}_{f'}) \\ &= \frac{3\beta}{m_{\alpha}} F_{\alpha}(\mathbf{r}_f; t') \delta_{\alpha\gamma} \delta(\mathbf{r}_f - \mathbf{r}_{f'}), \end{aligned} \quad (49)$$

where

$$F_{\alpha}(\mathbf{r}_f; t') = \left\langle \sum_{j=1}^{N_{\alpha}} \delta(\mathbf{r}_f - \mathbf{r}_j) \right\rangle_{\varphi}^{t'} \quad (50)$$

is the quasiequilibrium unary distribution function of ions of species α in the electrolyte solution calculated for quasiequilibrium state (14). Similarly, in function $\bar{D}_{jjn}^{\alpha\alpha'\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')$ the time correlation function $\langle (1 - P(t))\hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l)T_q(t, t')(1 - P(t'))\hat{\mathbf{j}}_{\alpha'}(\mathbf{r}_{l'})\hat{n}_{\alpha''}(\mathbf{r}_{l''}; t') \rangle_{\varphi}^{t'}$ can be calculated via the moments:

$$\begin{aligned} &\langle (1 - P(t))\hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l)T_q(t, t')(1 - P(t'))\hat{\mathbf{j}}_{\alpha'}(\mathbf{r}_{l'})\hat{n}_{\alpha''}(\mathbf{r}_{l''}; t') \rangle_{\varphi}^{t'} \\ &= D_{0jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t') e^{-\lambda_{jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')} (1 + B_{jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')), \end{aligned}$$

where at $l = f, l' = f', l'' = f''$ the zero moment has the following form:

$$\begin{aligned} D_{0jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t') &= \langle (1 - P(t))\hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l)(1 - P(t'))\hat{\mathbf{j}}_{\alpha'}(\mathbf{r}_{l'})\hat{n}_{\alpha''}(\mathbf{r}_{l''}; t') \rangle_{\varphi}^{t'} \\ &= \frac{3\beta}{m_{\alpha}} F_{\alpha\alpha''}(\mathbf{r}_f \mathbf{r}_{f''}; t') \delta_{\alpha\alpha'} \delta(\mathbf{r}_f - \mathbf{r}_{f'}). \end{aligned} \quad (51)$$

Here, $F_{\alpha\alpha''}(\mathbf{r}_f \mathbf{r}_{f''}; t')$ is the quasiequilibrium pair distribution function of ions of species α, α'' in the electrolyte solution calculated for quasiequilibrium state (14). $\lambda_{jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')$ is the normalized second moment and $B_{jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')$ is a function including higher moments of the corresponding correlation function $\langle (1 - P(t))\hat{\mathbf{j}}_{\alpha}(\mathbf{r}_l)T_q(t, t')(1 - P(t'))\hat{\mathbf{j}}_{\alpha'}(\mathbf{r}_{l'})\hat{n}_{\alpha''}(\mathbf{r}_{l''}; t') \rangle_{\varphi}^{t'}$. Thus, the diffusion coefficients in quasiequilibrium state (14) are expressed via unary quasiequilibrium distribution functions $F_{\alpha}(\mathbf{r}_f; t')$, and $D_{0jjn}^{\alpha\alpha'\alpha''}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')$ — via the pair quasiequilibrium distribution functions $F_{\alpha\alpha''}(\mathbf{r}_f \mathbf{r}_{f''}; t')$, which, obviously, should be calculated based on quasiequilibrium statistical operator (14). In this case, a method of functional integration [42,43] can be implemented. This allows one to obtain quasiequilibrium unary and pair distribution functions for ions and electrons in the “electrolyte — electrode” system with taking into account a specific character of short-range and long-range interactions between particles in electrolyte (classical description) and in electrode (quantum description) as well as at their interface. For calculation of quantum “ion-ion”, “ion-electron” and “electron-electron” diffusion coefficients a method of moments can be used as well. However, in our opinion, here the tunneling processes, effective interactions inside the electrode structure should be considered based on quantum models like in Ref. [31].

6. Conclusions

Summarizing, we proposed a statistical theory of classical-quantum description of electrodiffusion transport processes of ions and electrons in the “electrolyte — electrode” system using the NSO method. The presented theory takes the spatial heterogeneity and memory effects into account. The model and

corresponding Hamiltonian are formulated and the nonequilibrium statistical operator for the “electrolyte — electrode” system as the functional of the corresponding parameters of the reduced description of the nonequilibrium processes (observable parameters) is obtained. In this approach, we receive the generalized transport equations such as Nernst-Planck equation for electrons and ions in the “electrolyte — electrode” system using the method of nonequilibrium statistical operator. These equations take into account the time memory effects and spatial heterogeneity. An important contributions to the generalized Nernst-Planck type equations are provided by the transport kernels $\bar{D}_{jjn}^{\alpha\alpha'\gamma}(\mathbf{r}_l, \mathbf{r}_{l'}, \mathbf{r}_{l''}; t, t')$ which, unlike the generalized diffusion coefficients, are the third-order correlation functions and enter into equations via terms of second order in the parameters $\varphi(\mathbf{r}_{l'}; t')\delta n_\gamma(\mathbf{r}_{l''}; t')$, $\varphi(\mathbf{r}_{l'}; t')\delta \bar{n}_e(\mathbf{r}_{s'}; t')$, $\varphi(\mathbf{r}_{s'}; t')\delta n_\gamma(\mathbf{r}_{l'}; t')$ which describe the dynamic correlations between the field and a density. We also obtained the system of equations for the flows of ions and electrons from which the conditions of the existence of stationary processes can be determined. Approximate calculation of diffusion coefficients by means of the method of moments in Gaussian approximation provides us the relationship between the unary and pair distribution functions of quasiequilibrium state (14) which, as it was mentioned, can be calculated using a method of functional integration [42,43]. An important open issue consists in the appearance of bound states of Li ions with electrons and Li ions inside electrode. For description of such processes, the transport equations should be complemented with the equations for “ion-ion”, “ion-electron” and “electron-electron” nonequilibrium pair distribution functions within the electrode structure. These problems we will consider in our future works. Besides, within the classical description of an electrolyte we did not consider explicitly polar molecules of solvent which, evidently, can significantly effect the polarization processes due to their orientational movement and can be transported into the porous structure of electrode (what leads to a decrease of porosity and cleavage). This needs a separate study as well.

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Статистичний опис електродифузійних процесів інтеркаляції іонів в системі “електроліт-електрод”

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Запропоновано статистичну теорію класично-квантового опису електродифузійних процесів інтеркаляції в системі “електроліт-електрод”. Отримано узагальнені рівняння Нернста-Планка для іонів та електронів в системі “електроліт-електрод”, використовуючи метод нерівноважного статистичного оператора. Отримані рівняння переносу враховують ефекти пам'яті в часі та просторову неоднорідність. Проведено аналітичні обчислення просторово неоднорідних коефіцієнтів дифузії в межах класичного опису.

Ключові слова: інтеркаляція, електро-дифузійний процес, рівняння переносу, нерівноважний статистичний оператор

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