

MODEL OF CONDUCTIVITY AND THE STRUCTURE OF THE SPACE CHARGE IN SOLID ELECTROLYTES

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1. In single crystals of most well-known solid electrolytes [1], only ions of one charge (normally cations) are mobile. The unipolar character of the conductivity of solid electrolytes may be different from the conductivity of defective crystals. In solid electrolytes we are clearly dealing with a "phase" which contains the highly mobile carriers. This treatment corresponds to the model of a uniform "cationic liquid" impregnating the rigid shell formed by immobile anions (and possibly by some immobile cations) [2]. Another treatment involves models which are analogous to those used in the description of conductivity involving Frenkel's defects. It is based on assumptions relating to the existence of a few types of states in which the cations can exist. These are deep "lattice sites" and shallow "interstitial positions"; the mobility associated with hopping of the cations along the interstices is characterized by very small activation energies. In this approach, the difference between the solid electrolytes and normal ionic crystals has a mainly qualitative character; it is assumed that in the solid electrolytes the number of interstitial positions is significantly greater but that they are shallower. The special feature of a solid electrolyte is related to the character of the collective interaction between the interstitial cations. It is therefore believed that the change to a high-conductivity state is not expressed in the structural phase change which "generates" a large number of fairly shallow positions available to the cations but by the step-like hopping redistribution of the cations between the "pre-existing" lattice sites and the interstitial positions [8]. In the first type of model it is assumed that the exchange between the various permitted crystal-chemical states is so intense that the cations can be considered as a uniform liquid (at least in considering those phenomena whose characteristic frequencies are much slower than the exchange frequencies); the transition to the high-conductivity state is provided by the transformation of the crystal lattice into a structure with a large number of positions available for the cations. The second type of model postulates the existence of well defined independent states for cations in the crystals lattice. In the present paper we have confined ourselves to a discussion of the uniform models.

2. In the case of the unipolar current model, the transport equation has the following form (within the framework of nonequilibrium thermodynamics [5]):

$$j/e = -D\nabla c + \sigma E/e. \quad (1)$$

The values of the diffusion coefficient D and the conductivity coefficient σ do not characterize an individual cation but a flow of cations arising as a result of the total concentration gradient of mobile cations ∇c and under the effect of the electric field E in the medium. The linear relationship between the flow and the thermodynamic force has often been used to describe the electric current in doped semiconductors and electrolyte solutions; it was normally assumed that D does not depend on the concentration while $\sigma \sim c$. It is obvious that if we take into account the interaction between the cations we obtain a concentration-dependent diffusion coefficient and a more complex dependence of σ on c . Thus, for example, in electrolyte solutions with a high concentration there are corrections to the "conductivity at infinite dilution" to take into account the forces of long-range interaction between the ions [4]. With an increase in the concentration, the short-range forces also become important. For the same reasons we must also expect a nonlinear $\sigma(c)$ dependence in solid electrolytes where, with high concentrations of mobile cations, the dependence will be determined in the first place by the short-range repulsion forces.

It is obvious that there is a maximum local concentration of cations c_m which can simultaneously be placed in the regular sublattice. The value of c_m is certainly limited by geometrical factors determined by the composition of the shell and the dimensions of the cations. Moreover, c_m can be decreased by the electrostatic

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repulsion between the cations. With cation concentrations close to the limiting concentration the migrational flow becomes proportional to the "hole" concentration, $c_m - c$. Thus, when $c \rightarrow 0$, $\sigma \sim c$ and when $c \rightarrow c_m$, $\sigma \sim c_m - c$. When $c \rightarrow 0$, $D \rightarrow D_0$ which is the "single-particle" diffusion coefficient of the cations. When $c \rightarrow c_m$, $D \rightarrow D_h$ which is the diffusion coefficient of holes and the diffusive flow decreases since the concentration gradient tends to zero. The dependence $\sigma(c)/D(c)$ can be analyzed using nonequilibrium thermodynamics. Let us now introduce the free-energy density of the system F and the electrochemical potential of the cations $\mu = \partial F / \partial c$:

$$F = F(c, \Phi) = ce\Phi + F_0(c); \quad \mu = e\Phi + \mu_0(c); \quad \mu_0 = F_0'(c), \quad (2)$$

where $F_0(c)$ is the free energy in the absence of an external field and Φ is the potential of the self-consistent field acting on the cation. In the linear approximation [5] we have, in the absence of a temperature gradient,

$$\frac{1}{e} \mathbf{j} = -[L(c)/kT] \nabla \mu = \{e\mathbf{E} - \mu_0'(c) \nabla c\} L(c)/kT. \quad (3)$$

Comparing Eq. (3) with (1), we see that $\sigma(c) = e^2 L(c)/kT$ and

$$f(c) = \sigma(c)/eD(c) = e\{\mu_0'(c)\}^{-1}, \quad (4)$$

i.e., in order to obtain $f(c)$ it is sufficient to have the expression for $\mu_0'(c)$ which can be considered on the basis of equilibrium microscopic models.

Let us look at a model of a lattice gas as an example: there are N noninteracting cations which can be arranged among N_m equivalent sites in the lattice. The specific free energy in this case has the form

$$F_0(N) = F_{00} - (kT/V) \ln \{N_m! [N!(N_m - N)!]^{-1}\},$$

where V is the volume of the system and F_{00} is a term proportional to N . Let us use the Stirling formula and introduce $c = N/V$ and $c_m = N_m/V$. Then

$$\text{const} + \mu_0(c) = kT \{\ln c - \ln(c_m - c)\}; \quad f(c) = c(1 - c/c_m) e/kT. \quad (5)$$

The collective interaction between the cations can lead to a marked difference in $\mu(c)$ from Eq. (5) in the region of intermediate concentrations. At the same time we should expect that Eq. (5) correctly describes the behavior of $f(c)$ in the region of low c and also in the case of c which is close to the limit. Therefore we can write $f(c)$ in the form

$$f(c) = c(1 - c/c_m) \xi(c) e/kT, \quad (6)$$

where $\xi(c)$ is a smooth function which does not go to zero when $0 \leq c \leq c_m$.

Equation (6) will be used later to study the structure of the equilibrium space charge in a solid electrolyte. Simple analytical results can be obtained with $\xi(c) = \xi = \text{const}$.

3. The field E is connected with the concentration c by Poisson's equation and as a result of the relationship of Eq. (3) under equilibrium conditions ($\mathbf{j} = 0$): $\epsilon \text{div } \mathbf{E} = 4\pi e(c - c_0)$; $f(c) \mathbf{E} = \nabla c$, where ϵ is the effective dielectric constant of the system. In a one-dimensional system (assuming $\Phi = 0$ in the electrically neutral region where $c = c_0$) the solution of these equations can be written in the form

$$e\Phi = -\varphi(c)kT; \quad E^2 = 8\pi kT c_0 \epsilon^{-1} [\bar{\varphi}(c) - \varphi(c)], \quad (7)$$

where

$$\varphi(c) = \frac{e}{kT} \int_c^c \frac{dc}{f(c)}; \quad \bar{\varphi}(c) = \frac{e}{kT} \int_{c_0}^c \frac{c dc}{c_0 f(c)}. \quad (8)$$

The distribution of potential and concentration along the x axis on the right of the equipotential plane $x = 0$ with a specified potential Ψ is found using the system of equations (7) which specify the dependences $\varphi(c)$ and $E(c)$, i.e., $E(\Phi)$ and therefore $\Phi(x)$. The characteristic space charge associating the potential Ψ with the surface charge density Σ on the $x = 0$ plane is the specific differential capacitance

$$C(\Psi) = d\Sigma/d\Psi = (\epsilon/4\pi) dE/d\Phi|_{\Phi=\Psi}.$$

Using Eqs. (7) and (8) we can express this in the form

$$C(\Psi) = C_0 |1 - c(\Psi)/c_0| \cdot [2\{\bar{\varphi}[c(\Psi)] + e\Psi/kT\}]^{-1/2}, \quad (9)$$

where the dependence $c(\Psi)$ is determined from the relationship of Eq. (7) while $C_0 = \epsilon/4\pi L_D$; $L_D = (\epsilon kT)^{1/2} (4\pi e^2 c_0)^{-1/2}$.

4. In a simple unipolar model which does not allow for saturation effects, $f = ec/kT$, $\varphi = \ln c/c_0$, and $\tilde{\varphi} = -1 + c/c_0$. Then from Eq. (7) it follows that $c = c_0 \exp\{-e\Phi/kT\}$. In the case of the capacitance, we obtain in accordance with Eq. (9) the well known result [6, 7] where $C(\Psi) = C(0) [1 - \exp\{-e\Psi/kT\}] \{2 [e\Psi/kT - 1 + \exp(-e\Psi/kT)]\}^{-1/2}$; $C(0) = C_0$.

5. In order to study the saturation effect in an analytical form, we use Eq. (6) with $\xi(c) = \xi = \text{const}$ and in this case we introduce the term $c_m = \nu c_0$, where $\nu > 1$. Then $\tilde{\varphi} = \xi^{-1} \ln\{c(\nu-1)/(c_0\nu-c)\}$; $\varphi = \xi^{-1} \nu \ln\{c_0(\nu-1)/(c_0\nu-c)\}$. Substituting in Eqs. (7) and (9) we obtain

$$c = c_0 \{1/\nu + (1-1/\nu) \exp[\xi e\Phi/kT]\}^{-1},$$

$$C(\Psi) = \frac{C(0) \sqrt{1-1/\nu} |1 - \exp(-\xi e\Psi/kT)|}{[1-1/\nu + 1/\nu \exp(-\xi e\Psi/kT)]} \times \frac{1}{\sqrt{2}} \{\xi e\Psi/kT + \nu \ln[1-1/\nu + 1/\nu \exp(-\xi e\Psi/kT)]\}^{-1/2}, \quad (10)$$

where the linear differential capacity $C(0) = C_0 \sqrt{\xi(1-1/\nu)} = \varepsilon/4\pi \tilde{L}_D$; $\tilde{L}_D = L_D [\xi(1-1/\nu)]^{-1/2}$. Within the limit $\nu \rightarrow \infty$ (and $\xi = 1$) these formulae change into the result in section 4. In accordance with Eq. (10), the capacitance is described by a curve with a maximum, which diminishes by a square root law in the region of large negative and positive potentials. The position of the maximum depends on the value of the parameter ν .

6. The qualitative results obtained here do not depend fundamentally on the choice of an approximation for $\xi(c)$. They are determined by the limiting properties of $f(c)$. For example, the limiting dependence of the capacitance $C(\Psi) \sim |\Psi|^{-1/2}$ is the consequence of the limitations on the local charge concentration $\rho = e(c - c_0)$; $\rho_{\min} < \rho < \rho_{\max}$ [in our model $\rho_{\min} = -ec_0$ and $\rho_{\max} = e(\nu-1)c_0$]. Indeed, close to the boundary with the surface charge, a layer of space charge is formed whose total value in the calculation is $-\Sigma$ for unit cross-sectional area. With sufficiently high negative Σ in a considerable portion of the layer, ρ is close to its own limiting value, the constant $\rho_{\max}$. The characteristic layer thickness is $l \approx -\Sigma/\rho_{\max}$. The field E decreases linearly: $\varepsilon dE/dx \approx 4\pi\rho_{\max}$, $E \approx (4\pi/\varepsilon)\rho_{\max}(x-l)$. Hence we find the connection between the potential Ψ and the charge Σ : $\Psi \approx -(2\pi/\varepsilon)\rho_{\max}l^2 = -2\pi\Sigma^2/\varepsilon\rho_{\max}$, i.e., $\Sigma(\Psi) \approx -\sqrt{\rho_{\max}|\Psi| \cdot \varepsilon/2\pi}$, $C(\Psi) = -d\Sigma/d\Psi \approx (\varepsilon\rho_{\max}/8\pi|\Psi|)^{1/2}$. Analogously, the density ρ in the case of large positive Σ inside the space charge reaches a constant minimum possible value $\rho_{\min}$, $l \approx \Sigma/\rho_{\min}$, and $C(\Psi) \approx (\varepsilon|\rho_{\min}|/8\pi\Psi)^{1/2}$. Thus the upper and lower limit to the local concentration of charge leads to saturation effects on both sides of the zero-charge point.* The composition between them determines the position of the maximum capacitance corresponding to the minimum characteristic thickness of the space charge (away from the zero-charge point $l \sim \sqrt{|\Psi|}$). When $|\rho_{\max}| > |\rho_{\min}|$ ($\nu > 2$), the negative asymptotic capacitance goes higher, i.e., the maximum $C(\Psi)$ must be shifted towards negative potentials. When $|\rho_{\max}| < |\rho_{\min}|$ ($\nu < 2$), the positive branch goes higher and the maximum lies in the region of positive potentials. When $|\rho_{\max}| \approx |\rho_{\min}|$ ($\nu \approx 2$), we can expect $C(\Psi)$ to be symmetrical in relation to $\Psi \approx 0$.†

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LITERATURE CITED

1. Fast Ion Transport in Solids, North Holland Publishing Co., Amsterdam (1973).
2. E. A. Ukshe and N. G. Bukun, *Élektrokhimiya*, **8**, 163 (1972).
3. Yu. Ya. Gurevich and Yu. I. Kharkats, *Dokl. Akad. Nauk SSSR*, **229**, 367 (1976).
4. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York (1958).
5. S. R. deGroot and P. Mazur, *Non-Equilibrium Thermodynamics*, North Holland, Amsterdam (1962).
6. V. A. Myamlin and Yu. V. Pleskov, *The Electrochemistry of Semiconductors* [in Russian], Nauka, Moscow (1965).
7. A. A. Kornyshev and M. A. Vorotyntsev, *Phys. Status Solidi* (a), in press.
8. Yu. Ya. Gurevich, *Dokl. Akad. Nauk SSSR*, **222**, 143 (1975).

* This result was obtained in [3] for one concrete model of a solid electrolyte.

† Starting from Eqs. (6) and (7) it is possible to show that the dependence $\xi(c)$ determines the constants in the corrections of the next order of smallness to these limiting laws. However, the form of $\xi(c)$ can affect the position of the maximum capacitance [in particular the asymmetry of $\xi(c)$ can lead to the situation where the curve $C(\Psi)$ at $\nu = 2$ will not be symmetrical].