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The influence of ion–ion interactions on the kinetics of intercalation in a layered host structure

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A mathematical model of cation intercalation in a layered host lattice is presented. Theoretical potential-time curves for galvanostatic charge-discharge and current-potential curves in linear sweep voltammetry are calculated for the case of cylindrical diffusion including the influence of ion–ion interactions and at the surface of the material. A kinetic analysis of the model behaviour is proposed.

Nomenclature

a	interaction energy
a'	interaction energy at the surface
b	interaction coefficient
C	concentration of intercalated specie
C^0	maximum concentration
D	diffusion coefficient
D^0	auto diffusion coefficient
E	electrochemical potential
E^0	standard electrochemical potential
i^*	dimensionless current density
i^*_{pa}	dimensionless anodic peak current density
i^*_{pc}	dimensionless cathodic peak current density
J	diffusion flux
k_a	anodic kinetic constant
k_c	cathodic kinetic constant
$\frac{1}{2}K^0nFC^0$	exchange current density (i^0)
L	material thickness (cylinder radius)
n	stochiometric number of electrons
d	dimensions of the diffusion space
r	cylinder radius variable
v	potential sweep rate
V	dimensionless potential
V^*_{pa}	dimensionless anodic peak potential
V^*_{pc}	dimensionless cathodic peak potential
y	intercalation ratio
α	transfer coefficient
ΔG_a	anodic free energy
ΔG_c	cathodic free energy
μ_{M+}	chemical potential
τ	maximum discharge time

1. Introduction

The intercalation of alkali metals in host structures has been widely investigated both in terms of kinetics and thermodynamics. For the latter, theoretical and experimental results coincide fairly well. This is, however, not the case for kinetics, for which the simple model generally used [1–4] fails to correlate theory and experiments. Previous models of the intercalation electrode have taken account of ion–ion interactions [5–8] and one of these models, proposed by Li Yongfang *et al.* [8] includes ion-lattice interactions. In all cases, the interface could be compared to an interface with adsorbed species with an interaction term [9]. The kinetic behaviour of the interface with adsorption has been given in a paper of Angerstein-Kozlowa *et al.* [9] in the case of linear sweep voltammetry. Atlung *et al.* [5–7] have only taken account of ion–ion interactions, and this solely for the special case of titanium disulphide under galvanostatic discharge.

We have extended this last study through the use of another important method: linear sweep voltammetry.

2. Theoretical study

The model of the influence of ion–ion interactions on intercalation kinetics is based on the work of Armand [1]. The chemical potential of an alkaline metal M^+ in a host structure is given by

$$\mu_{M+} = \mu^0_{M+} + RT\ln(y/1-y) + ay \qquad (1)$$

where a is the mean interaction energy between nearest neighbour ions, y the intercalation ratio and the standard state is $y^0 = 0.5$ according to [8].

The chemical poential of M^+ in the electrolyte [2] can be considered a constant if the concentration and the diffusion coefficient of M^+ are high.

Assuming that migration and convection fluxes are negligible, the flux is reduced to 'diffusion flux'

$$J = -C^0D\,\partial y/\partial r \qquad (2)$$

where $D = D^0(1 + ay(1-y)/RT)$ is the apparent diffusion coefficient and D^0 the diffusion coefficient without ion–ion interactions.

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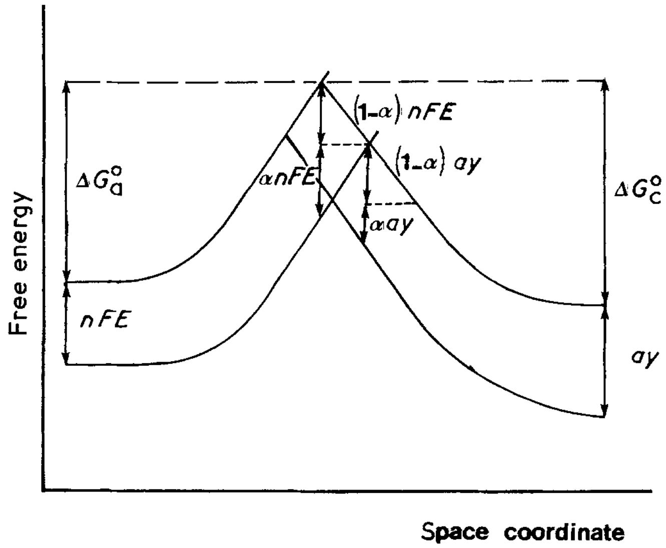

Fig. 1. Free energy against space coordinate for identical interaction energy at the surface and in the bulk of the material.

Mass conservation is expressed via:

$$C^0\frac{\partial y}{\partial t} = -\frac{1}{r^{d-1}}\frac{\partial}{\partial r}(r^{d-1}J) \tag{3}$$

where d is the dimension of the diffusion space.

In the case of a lamellar host structure like titanium disulphide, using Atlung's model [5] of cylindric grains with a radius L for a composite electrode, the value of d is 2 and equation (3) becomes:

$$\frac{\partial y}{\partial t} = D\left(\frac{1}{r}\frac{\partial y}{\partial r} + \frac{\partial^2 y}{\partial r^2}\right) + D^0\left(\frac{a(1-2y)}{RT}\right)\left(\frac{\partial y}{\partial r}\right)^2 \tag{4}$$

The boundaries and initial conditions are as follows:

At the material centre, we apply the symmetry condition

$$r\frac{\partial y}{\partial r} = 0 \tag{5}$$

Several possibilities were examined for mass conservation at the electrode interface. For a material in which the ions are not subjected to any interaction, the free energy changes for the transfer from the electrolyte to the material (and the reverse process) are expressed as

$$\Delta G_c = \Delta G^0_c + \alpha nFE \tag{6a}$$

$$\Delta G_a = \Delta G^0_a - (1-\alpha)nFE \tag{6b}$$

Application of the Arrhenius relationship to the kinetic constant gives

$$k_c = k^0_c \exp\left(-\alpha\frac{nFE}{RT}\right) \tag{7a}$$

$$k_a = k^0_a \exp\left((1-\alpha)\frac{nFE}{RT}\right) \tag{7b}$$

and the current density is given by

$$i = nFK^0C^0\left\{y\exp\left[(1-\alpha)\frac{nEV}{RT}\right] - (1-y)\exp\left[-\alpha\frac{nEV}{RT}\right]\right\} \tag{8}$$

where $V = E - E^0 = -(\mu_{M+} - \mu^0_{M+})/F$ at the interface and the exchange current density (at the standard state) is given by

$$\log i^0 = \tfrac{1}{2}nFK^0C^0 \tag{9}$$

When ion–ion interactions are involved in the host material, the free energy is reduced by a value ay in the cathode and, if the interactions have the same effect on the surface and inside, the corresponding energy is shared with the same coefficients α and $(1-\alpha)$ as the nFE term [9]

$$\Delta G_c = \Delta G^0_c + \alpha ay + \alpha nFE \tag{10a}$$

$$\Delta G_a = \Delta G^0_a - (1-\alpha)(nFE - ay) \tag{10b}$$

and the current density is expressed as

$$i = nFK^0C^0\left\{y\exp\left[(1-\alpha)\frac{(nFV+ay)}{RT}\right] - (1-y)\exp\left[-\alpha\frac{(nFV+ay)}{RT}\right]\right\} \tag{11}$$

In the case of linear sweep voltammetry, the potential is given by:

$$V = E - E^0 = V^0 \pm vt \tag{12}$$

and if the initial potential V^0 is sufficiently high, the initial value of y can be assumed to be zero. In the constant current method, the initial value of y can also be assumed to be zero.

This differential equation was solved using an implicit finite difference method (Crank-Nicholson). To facilitate the solving of our system, we have used the adimensional variables shown in Table 1.

3. Results and discussion

3.1. *Galvanostatic discharge*

Typical curves for constant current discharges (for a given current density and a given cylinder radius) are shown in Fig. 2. Whatever the current intensity and the cylinder radius, the coulombic efficiency increases with the term $b = a/RT$. The potential, on the other

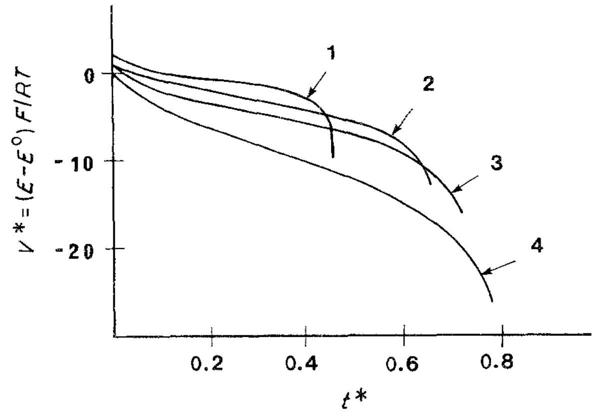

Fig. 2. V^* against t^* for: 1 ($b = 0$), 2 ($b = 5$), 3 ($b = 10$) and 4 ($b = 20$), with $L^* = \sqrt{5}$.

hand, falls more rapidly. The dimensionless variable $F(E - E^0)/RT$ permits demonstration of the real influence of the interaction term, as on experimental curves.

This can be explained by the fact that the ions on the surface tend to move into the material under the effect of two forces: the concentration gradient due to the constant current density, which forces the ions to enter the material and the ionic repulsion forces which facilitate a more homogeneous filling of the material. This second force cannot act in the direction of the surface because of the opposite force of the concentration gradient.

The result is an increase of the coulombic efficiency. On the other hand, the energy provided to the ions decreases the potential of the system accordingly: for the same amount of intercalated ions, the interfacial concentration is lower and the voltage higher, in the case of an homogeneous distribution of the ions, than in the case of a high concentration gradient. But this effect on the potential is overcompensated by the term ay/F which decreases the value of E.

We have represented the coulombic efficiency as a function of the ratio $\tau D/L^2 = 1/L^{*2}$ for different interaction coefficient values (Fig. 3). This set of curves shows the increase of the coulombic efficiency with

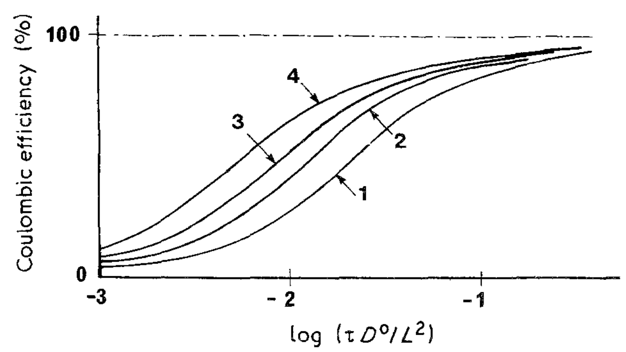

Fig. 3. Coulombic efficiency against the ratio log ($\tau D^0/L^2$) for: 1 ($b = 0$), 2 ($b = 5$), 3 ($b = 10$) and 4 ($b = 20$).

the interactions. In addition, it shows the error made when the $b = 0$ curve is used to determine the diffusion coefficient, D^0, in a material in which there are interactions. The calculated value is higher than D^0. If, on the other, the interactions are taken into account, the difference between the diffusion coefficient measured by electrochemical means, and that measured by another method (e.g. RMN) is reduced. For an interaction coefficient of 20, for example, the diffusion coefficient, D^0, is approximately a quarter of the value measured without taking into account interactions.

3.2. *Cyclic voltammetry*

3.2.1. Reversible transfer. Interactions have a twofold effect on the voltammetric curves. The peak current becomes smaller in magnitude and broader in shape as the interactions increase and the reduction peak potential shifts towards more negative potentials (Fig. 4). It is important to note that the dimensionless variable V^*, as in the case of galvanostatic discharge, gives the representation of the voltammetric curves as in the experimental measurements with respect to a reference electrode and not referred to a standard state.

However, the position of the oxidation peak varies according to the dimensionless cylinder radius (L^*)

Table 1.

Variable	*Dimensionless variable*	
	Cyclic voltammetry	*Constant current*
Space (r)	$r^* = r\left(\frac{Fv}{RTD^0}\right)^{1/2}$	$r^* = \frac{r}{(\tau D^0)^{1/2}}$
	$L^* = L\left(\frac{Fv}{RTD^0}\right)^{1/2}$	$L^* = \frac{L}{(\tau D^0)^{1/2}}$
Time (t)	$t^* = \frac{Fvt}{RT}$	$t^* = \frac{t}{\tau}$
Interaction coefficient (b)	$b = \frac{a}{RT}$	$b = \frac{a}{RT}$
current density (i)	$i^* = \frac{i}{FC^0}\left(\frac{RT}{FvD^0}\right)^{1/2}$	$i^* = \frac{i}{FC^0}\left(\frac{\tau}{D^0}\right)^{1/2}$
voltage (V)	$V^* = F\frac{(E - E^0)}{RT}$	$V^* = F\frac{(E - E^0)}{RT}$
Initial voltage (V^0)	V^{0*}	

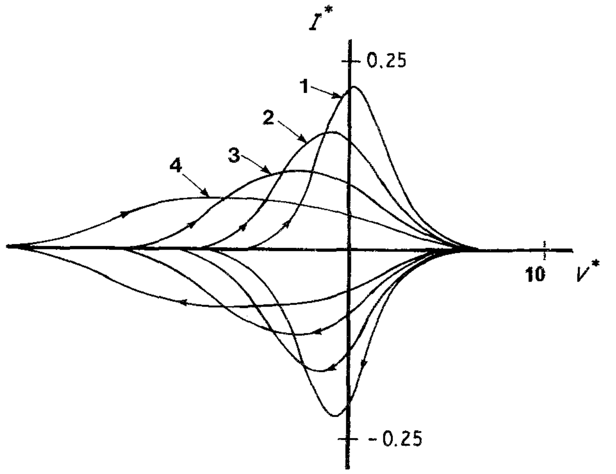

Fig. 4. I^* against V^* for $L^* = 2.25$ for: 1 ($b = 0$), 2 ($b = 2$), 3 ($b = 5$) and 4 ($b = 10$).

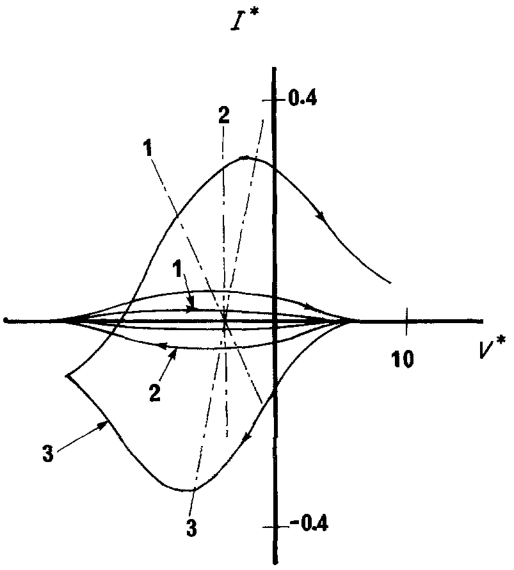

Fig. 5. I^* against V^* for $b = 10$ and with: 1 ($L^* = 10$), 2 ($L^* = 2.25$) and 3 ($L^* = 4$).

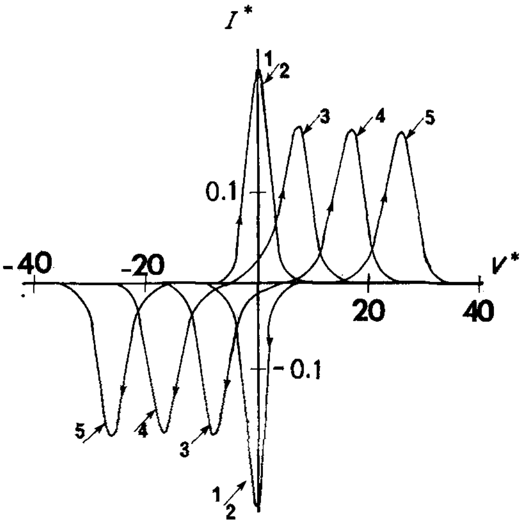

Fig. 6. Influence of the irreversibility on I^* against V^* curves for $L^* = 2.25$, $b = 0$, $\alpha = 0.5$ and for: 1 ($(K^0(RTF/D^0v)^{1/2} = 10^4)$), 2 ($10^2$), 3 ($10^{-2}$), 4 ($10^{-4}$) and 5 ($10^{-6}$).

of the material (Fig. 5). The dimensionless cylinder radius L^* in fact represents three parameters: the real cylinder radius, the diffusion coefficient, D^0, and the potential sweep rate. Large values of L^* correspond to semi-infinite diffusion conditions and very small L^* values correspond to homogeneous diffusion [2].

The value $V^*_{\text{pa}} - V^*_{\text{pc}}$ as a function of L^*, therefore, passes through a minimum (negative). For L^* near zero (not represented on Fig. 5), the forward and reverse peak potentials have the same value, depending on the energy value, b. Furthermore, in this case it is possible to calculate the adimensional peak currents and potentials:

$$i^*_{\text{pa}} = i^*_{\text{pc}} = \frac{1}{2}\frac{L}{(4 + b)}$$

$$V^*_{\text{pa}} = V^*_{\text{pc}} = -\tfrac{1}{2}b$$

For higher values of L^*, i.e. higher values of L and/or smaller values of D^0 and/or faster potential speed, the oxidation peak appears at more negative potentials than the reduction peak (Fig. 5, curve 1).

If the material is very thick and/or D^0 very small and the potential speed very fast, the distance between the peaks becomes positive again (Fig. 5, curve 3).

These variations of the peak potentials can be explained by using an example of variations of L^* related only with L (v and D^0 fixed). The diffusion coefficient varies with the intercalation ratio, y, according to the equation $D = D^0(1 + by(1 - y))$. In the case of thick cylinders, the diffusion is semi-infinite and the degree of intercalation varies only in a thin layer, near the interface. The increase in D with y favours the intercalation (the maximum influence occurs for an interfacial value of $y = 0.5$, near the peak potential) but only towards the bulk of the electrode: in the reduction process, the interfacial potential forces the ions through the interface and the interactions have the same effect. For the following oxidation process, the interfacial potential now forces the ions to leave the material, enhanced by the interaction forces with a thin layer. In the bulk of the electrode, the same interactions help diffusion towards the opposite inner interface.

In the case of a very thin cylinder, any variation in y concerns the entire sample. In reduction, the intercalation is forced by the interfacial potential and the favourable effect of repulsive interactions is strongly limited by the cylinder radius. In oxidation, the potential forces the ions to leave the cylinder as do the interactions. The oxidation peak potential could then appear at more negative potential than the reduction peak, a quite remarkable result. This is the difference as compared with the semi-infinite case.

Table 2.

Equations

$$\frac{\partial y}{\partial t^*} = (1 + by(1 - y))\left(\frac{1}{r^*}\frac{\partial y}{\partial r^*} + \frac{\partial^2 y}{\partial r^{*2}}\right) + b(1 - 2y)\left(\frac{\partial y}{\partial r^*}\right)^2$$

initial and boundary conditions (linear sweep voltammetry with a reversible transfer):

$$\left.\begin{array}{ll} y = (1 - y)\exp(-V^* - by) & \text{for } r^* = L^* \\ r^*\dfrac{\partial y}{dr^*} = 0 & \text{for } r^* = 0 \end{array}\right\} \forall t^* = 0$$

$$y = (1 - y)\exp(-V^{0*} - by) \quad \text{for } t^* = 0 \quad \forall r^*$$

initial and boundary conditions (constant current method or linear sweep voltammetry with an irreversible transfer):

$$\left.\begin{array}{ll} i^* = (1 + by(1 - y))\dfrac{\partial y}{\partial r^*} & \text{for } r^* = l^* \\ r^*\dfrac{\partial y}{\partial r^*} = 0 & \text{for } r^* = 0 \end{array}\right\} \forall t^* = 0$$

$$y = (1 - y)\exp(-V^{0*} - by) \quad \text{for } t^* = 0 \quad \forall r^*$$

In the case of the constant current method, i^* = constant and in the case of linear sweep voltammetry with an irreversible process, i^* is a function of V^* according to Equations 8 and 11.

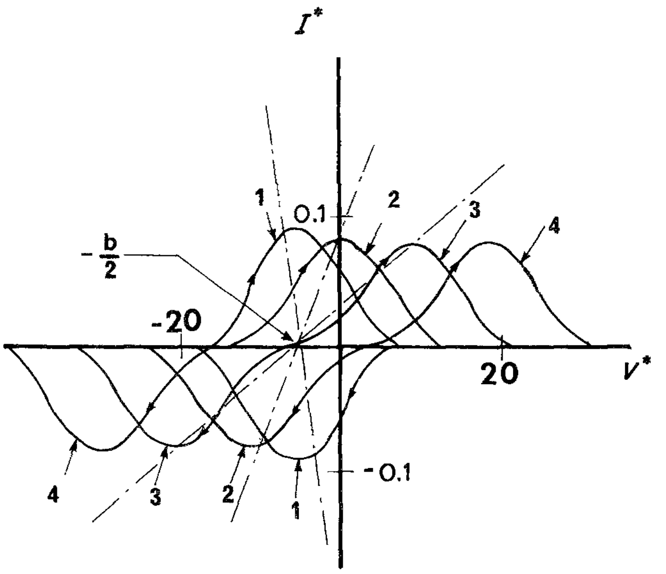

Fig. 7. Influence of the irreversibility on I^* against V^* curves for $L^* = 2.25$, $b = 10$, $\alpha = 0.5$ and for: 1 ($K^0(RTF/D^0v)^{1/2} = 1$), 2 (10^{-2}), 3 (10^{-4}) and 4 (10^{-6}).

3.2.2. Irreversible transfer. Charge transfer irreversibility increases the distance between reduction and oxidation peaks whether or not interactions are involved. If the interactions are identical on the surface and inside the reduction peak broadens and the maximum occurs at a more negative potential. The position of the middle point between the peak potentials is equal to $b/2$. Figures 6–7 show the influence of the dimensionless kinetic constant $K^* = K^0(RTF/D^0v)^{1/2}$ on the current potential curves. We can see that the peak current is constant for values of K^* higher than 1 (the process is reversible) and decreases sharply when K^* decreases to reach an almost constant value. This phenomenon is less apparent when interactions occurs.

The influence of L^* on the peak current is given in Fig. 8. For small values of L^*, the interactions strongly decreases the peak current: the interactions favour the filling and decrease the concentration gradient at the interface (and the current). In the case of semi infinite diffusion, for very high values of L^*, this influence is reversed but with very small variations. The local variations of y near the interface for $y \sim 0.5$ (the maximum of D) could result in higher gradients and currents.

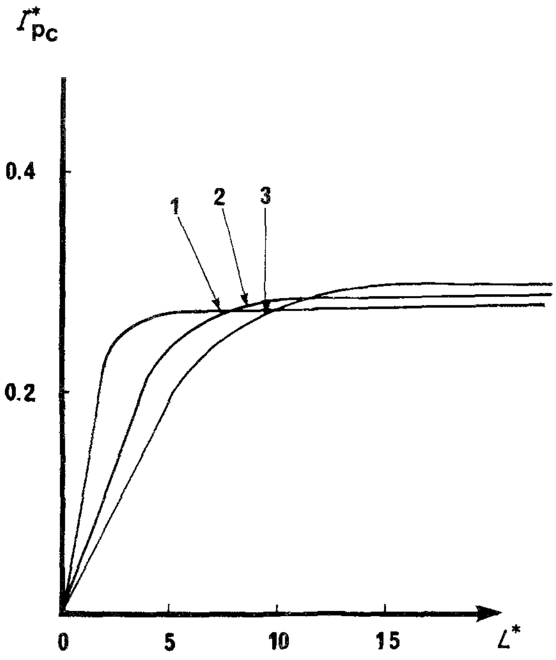

Fig. 8. Variations of the dimensionless cathodic peak current against L^* for $K^* = 10^{-4}$ and for: 1 ($b = 0$), 2 ($b = 5$) and 3 ($b = 10$).

4. Conclusion

The influence of repulsive ion–ion interactions in a layered intercalation material has been simulated in the case of cyclic voltammetry and galvanostatic discharge. The following features have been revealed:

(i) In the case of homogeneous diffusion (very thin cylindric grains, for example), the forces of repulsion favour greater spacing between ions, causing ions to leave the intercalation material. The final effect depends on the reaction process: a positive current increases this effect and a negative current decreases it. The anodic peak potential could be more negative than the cathodic peak potential.

(ii) In the case of semi-infinite diffusion, a great part of the repulsion forces favours the displacement of ions towards the bulk of the intercalated material.

(iii) The interactions increase the coulombic efficiency of the galvanostatic discharge. The measurements of the diffusion coefficient, D^0, by the use of the theoretical curves obtained without interactions gives an error. It is necessary to take account of the interaction coefficient b.

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