

SHORT COMMUNICATION

Milivoj Lovrić · Fritz Scholz

A model for the coupled transport of ions and electrons in redox conductive microcrystals

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Abstract Coupled diffusion of ions and electrons in microcrystals of insertion compounds immobilized at an electrode surface is theoretically analysed by a lattice-gas model without interactions. The transport in the direction perpendicular to the electrode surface depends on Wagner's factor for electrons, while the transport parallel to the electrode depends on this factor for ions. The iso-concentration profiles may depend on the orientation of the particle on the electrode surface. Chronoamperometric responses of volume and surface redox reactions are calculated.

Key words Solid state chronoamperometry · Coupled transport · Insertion electrodes

Introduction

Insertion compounds are solids exhibiting mixed ionic and electronic conductivity [1]. Their electrochemical properties can be measured by cyclic voltammetry if the microcrystals are mechanically transferred onto the surface of a graphite electrode [2–10]. The main characteristic of these redox reactions is the separation of fluxes: electrons are exchanged at the electrode |particle interface, while ions enter the crystal through the particle | solution interface. The most reactive zone is the three-phase boundary, where these two interfaces meet. In a previous paper [11], a theoretical model of a simple redox reaction with the insertion of cation C^+ was developed:



where $\{\text{Ox}\}$ and $\{C_n\text{Red}\}$ were insoluble components of the solid particle and the ion C^+ was dissolved in the liquid electrolyte. It was assumed that the insertion compound was not a metallic conductor, but that the mobility of the charge inside the particle was achieved by the electron hopping between localized redox sites and was accompanied by the diffusion of counterions C^+ , as in redox polymers [12]. This mechanism is called the faradaic, or redox, conductivity and it obeys Fick's laws of diffusion [13]. In the model it was assumed that the diffusion in the direction perpendicular to the electrode surface depended on the diffusion coefficient of the electrons, while the diffusion in the direction parallel to the electrode surface depended on the diffusion coefficient of the ions. In this short communication a rigorous model for the coupled diffusion of ions and electrons in two directions is developed using a lattice-gas concept without interactions, and the relationship between the diffusion coefficients is discussed.

Theory and discussion

In equilibrium, the reaction of Eq. (1) satisfies the Nernst equation:

$$[\text{Ox}] = [C_n\text{Red}] \exp(nF(E - E_f)/RT) \quad (2)$$

where E is the electrode potential and E_f is a formal potential which is defined as:

$$E_f = E^\circ + (RT/nF) \ln(K) + (RT/F) \ln[C^+] \quad (3)$$

Here E° is a standard potential of the redox reaction $\{\text{Ox}\} + ne^- \rightleftharpoons \{\text{Red}^{n-}\}$, and K is an equilibrium constant of the ion-transfer reaction $\{\text{Red}^{n-}\} + nC^+ \rightleftharpoons \{C_n\text{Red}\}$ [14]. The concentrations of the solid redox components $[\text{Ox}]$ and $[C_n\text{Red}]$ are equal to the product of the molar density of the solid compound (ρ) and the mole fraction of the particular component in the mixed

M. Lovrić (✉)
Center for Marine Research Zagreb,
"Ruder Bošković" Institute,
P.O.B 1016, 10001 Zagreb, Croatia

F. Scholz
E.-M. Arndt-Universität Greifswald
Institut für Chemie, Soldtmannstrasse 23,
D-17489 Greifswald, Germany

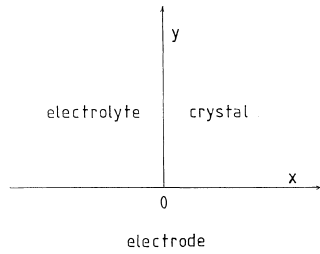


Fig. 1 A scheme of the theoretical model

crystal [15]. The concentration of the ions C^+ dissolved in the solution is assumed to be higher than 1 M, so that transport in the solution can be neglected [16].

The same geometric model as in the previous paper [11] is assumed: an infinite crystal attached to an infinite electrode surface (see Fig. 1). The positive semi-axis x is located in the crystal |electrode interface, and the negative semi-axis x lies in the liquid electrolyte|electrode interface. The positive semi-axis y is situated in the electrolyte|crystal interface. The three-phase boundary is perpendicular to the x - y plane. The Nernst equilibrium is initially established along this boundary. Then the current is conducted over the crystal surface which is facing the solution by the diffusion of electrons, because the ions from the solution can readily compensate for changes in charge arising from faradaic reactions there. This surface redox reaction creates a gradient of electrochemical potential and defines the initial conditions for the diffusion of ions into the crystal body. Hence, the ions do not penetrate the crystal surface only at the three-phase boundary and their diffusion in the crystal is not radial. The edge effects are neglected.

The fluxes of electrons and ions in the solid particle are mutually perpendicular and proportional to the gradients of the corresponding electrochemical potentials:

$$j_{(+)} = -D_{(+)}W_{(+)}(\partial c_{(+)}/\partial x) - D_{(+)}c_{(+)}|z_{(+)}|F(\partial\phi/\partial x)/RT \quad (4)$$

$$j_{(-)} = -D_{(-)}W_{(-)}(\partial c_{(-)}/\partial y) + D_{(-)}c_{(-)}|z_{(-)}|F(\partial\phi/\partial y)/RT \quad (5)$$

where $W = 1 + \partial \ln(\gamma)/\partial \ln(c)$ is Wagner's thermodynamic factor and γ is the activity coefficient [1]. If $z_{(-)} = -z_{(+)}$, the condition of electroneutrality requires that $j_{(+)} = j_{(-)}$ and $c_{(+)} = c_{(-)} = [CRed]$. The potential ϕ is caused by the charge separation. An uncompensated charge is surrounded by a spherical electric field, so that $\partial\phi/\partial x = \partial\phi/\partial y$. Under these conditions the potential gradient and the coupled flux are:

$$\begin{aligned} \partial\phi/\partial x = & (D_{(-)}W_{(-)}(\partial c/\partial y) \\ & - D_{(+)}W_{(+)}(\partial c/\partial x)) \\ & \cdot (D_{(-)} + D_{(+)})^{-1}(cF/RT)^{-1} \end{aligned} \quad (6)$$

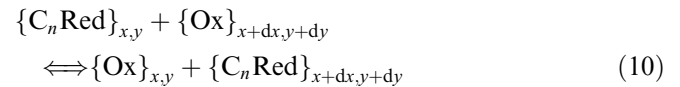
$$j = -D_x(\partial c/\partial x) - D_y(\partial c/\partial y) \quad (7)$$

$$D_x = D_{(-)}D_{(+)}W_{(+)}(D_{(-)} + D_{(+)})^{-1} \quad (8)$$

$$D_y = D_{(-)}D_{(+)}W_{(-)}(D_{(-)} + D_{(+)})^{-1} \quad (9)$$

The diffusion coefficients D_x and D_y differ by Wagner's factors. The physical meaning of this factor was recently discussed by Maser [17] who applied the concept of dopant-occupiable sites. Apparently, the factor is the consequence of the quasi-bimolecular nature of each singular electron, or ion transfer step.

It is well known [11, 17–20] that a series of electron and ion exchange reactions between immobile redox centers



results in the net charge transfer which obeys Fick's law of diffusion:

$$\begin{aligned} d[C_n \text{Red}]_{x,y}/dt = & k\rho(dx)^2(d^2[C_n \text{Red}]_{x,y}/dx^2) \\ & + k\rho(dy)^2(d^2[C_n \text{Red}]_{x,y}/dy^2) \end{aligned} \quad (11)$$

where k is a bimolecular rate constant, ρ is the molar density and dx and dy are mean distances between two adjacent redox sites. The products $k\rho(dx)^2$ and $k\rho(dy)^2$ correspond to the diffusion coefficients D_x and D_y , respectively. If the redox centers are not spherical, then $dx \neq dy$ and consequently $D_x \neq D_y$. This kinetic theory explains well the mechanism of electron hopping in redox polymers [13]. The consequence of its application to solid particles is that the diffusion coefficients D_x and D_y may depend on the orientation of the crystals on the electrode surface. This implies that the Wagner's factors for ions and electrons may depend on the crystal orientation, which is in the agreement with Maser's theory [17]. Equation 11 was derived by assuming that both ions and electrons are exchanged simultaneously and that no charge separation occurs. However, by identifying $k\rho(dx)^2$ and $k\rho(dy)^2$ with D_x and D_y (Eqs. 8 and 9), respectively, the influence of the spherical electric field (Eq. 6) is introduced in Eq. (11).

The propagation of the redox reaction of Eq. 1 through the crystal is described by the differential equation:

$$\partial[C_n \text{Red}]/\partial t = D_x \partial^2[C_n \text{Red}]/\partial x^2 + D_y \partial^2[C_n \text{Red}]/\partial y^2 \quad (12)$$

with the following initial and boundary conditions:

$$t = 0: [\text{Ox}] = \rho, \quad [C_n \text{Red}] = 0 \quad (13)$$

$$t > 0, \quad x \rightarrow \infty: [\text{Ox}] \rightarrow \rho, \quad [C_n \text{Red}] \rightarrow 0 \quad (14)$$

$$y \rightarrow \infty: [\text{Ox}] \rightarrow \rho, \quad [C_n \text{Red}] \rightarrow 0 \quad (15)$$

$$x \geq 0 \text{ and } y \geq 0: [\text{Ox}] + [C_n \text{Red}] = \rho \quad (16)$$

$$x = 0 \text{ and } y = 0: [\text{Ox}]_{x=0,y=0} = [C_n \text{Red}]_{x=0,y=0} \exp(\varphi) \quad (17)$$

$$\varphi = nF(E - E_f)/RT \quad (18)$$

$$x = 0: nFD_x(\partial[C_n\text{Red}]/\partial x)_{x=0} = -dI_s/dS \quad (19)$$

$$dS = b \cdot dy \quad (20)$$

$$y = 0: nFD_y(\partial[C_n\text{Red}]/\partial y)_{y=0} = -dI_a/dA \quad (21)$$

$$dA = b \cdot dx \quad (22)$$

where $S = b \cdot y$ and $A = b \cdot x$ are the areas of the crystal [electrolyte and the crystal] electrode interfaces, respectively, and b is the length of the three-phase boundary. The amounts of charges passing through these interfaces are equal. However, the areas of these two interfaces (S and A) do not have to be equal. So, the currents I_s and I_a are equal, but their densities I_s/S and I_a/A do not have to be equal. These densities depend on the diffusion coefficients D_x and D_y which need not be equal.

The solution of Eq. 12 for chronoamperometry is obtained by using the Laplace transformation and the substitution

$$\mathcal{L}[C_n\text{Red}] = P(x, s)Q(y, s) \quad (23)$$

Equation 12 is separated into two differential equations:

$$D_x(\partial^2 P(x, s)/\partial x^2) = \lambda s P(x, s) \quad (24)$$

$$D_y(\partial^2 Q(y, s)/\partial y^2) = (1 - \lambda)s Q(y, s) \quad (25)$$

where s is the transformation variable and λ is a constant defined as $0 < \lambda < 1$. At the constant electrode potential, the solution of Eqs. 24 and 25 is:

$$\mathcal{L}[C_n\text{Red}] = \rho(1 + \exp(\varphi))^{-1} s^{-1} \times \exp\left(-s^{1/2}\left(xD_1^{-1/2} + yD_2^{-1/2}\right)\right) \quad (26)$$

where $D_1 = D_x/\lambda$ and $D_2 = D_y/(1 - \lambda)$. The currents are calculated using Eq. 26 and the conditions of Eqs. 19–22. After the inverse Laplace transformation and the integration over the whole interface area one obtains

$$I_s = nFb\rho D_x(\pi D_1 t)^{-1/2}(1 + \exp(\varphi))^{-1} \times \int_0^\infty \exp(-y^2/4D_2 t) dy \quad (27)$$

$$I_a = nFb\rho D_y(\pi D_2 t)^{-1/2}(1 + \exp(\varphi))^{-1} \times \int_0^\infty \exp(-x^2/4D_1 t) dx \quad (28)$$

The integrals in eqs. 27 and 28 are equal to $(\pi D_2 t)^{1/2}$ and $(\pi D_1 t)^{1/2}$, respectively. From the condition $I_s = I_a = I$ it follows that $D_x(D_2/D_1)^{1/2} = D_y(D_1/D_2)^{1/2}$ and hence $\lambda = 0.5$. So the current and the concentration of the reduced redox component are:

$$I = nFb\rho(D_x D_y)^{1/2}(1 + \exp(\varphi))^{-1} \quad (29)$$

$$[C_n\text{Red}] = \rho(1 + \exp(\varphi))^{-1} \text{erfc}\left\{2^{-1}t^{-1/2}\left[x(2D_x)^{-1/2} + y(2D_y)^{-1/2}\right]\right\} \quad (30)$$

This is the same result as in the previous paper [11], but here it is obtained without intuitively assumed separation of the current into the surface and volume components. The steady-state current having the form of the polarographic wave (Eq. 29) is the consequence of the assumption that the crystal has an infinite volume.

The iso-concentration profiles are straight lines, which can be calculated from Eq. 30 by putting $x(2D_x t)^{-1/2} + y(2D_y t)^{-1/2} = 2\kappa$, where κ is a certain constant. This condition is satisfied if:

$$y = -(D_y/D_x)^{1/2}x + 2\kappa(2D_y t)^{1/2} \quad (31)$$

If $D_{(-)} = D_{(+)}$, the diffusion coefficients are: $D_x = DW_{(+)} / 2$ and $D_y = DW_{(-)} / 2$. Hence, D_x depends on Wagner's factor for ions and D_y depends on this factor for electrons. The actual concentration of the reduced component along the profile is: $[C_n\text{Red}] = \rho(1 + \exp(\varphi))^{-1} \text{erfc}\{\kappa\}$, which can be calculated by using the error function tables.

The surface of particles is in contact with the liquid electrolyte. It may exhibit the redox conductivity even if it cannot be penetrated by the ions C^+ (i.e., if $D_x = 0$). Under chronoamperometric conditions, the current on the surface can be calculated from the derivation of Eq. 28:

$$dI_a/dA = nF\rho D_y(D_2\pi t)^{-1/2}(1 + \exp(\varphi))^{-1} \times \exp(-x^2/4D_1 t) \quad (32)$$

The surface is located at $x = 0$. By putting $D_2 = 2D_y$ and $dA = b dx$, where dx is a thickness of molecular monolayer, the surface current is:

$$I_{a,x=0} = nF\rho b dx(D_y/2\pi t)^{1/2}(1 + \exp(\varphi))^{-1} \quad (33)$$

Contrary to the volume current (see Eq. 29), the current on the particle surface decreases with the square-root of time and depends solely on the surface diffusion coefficient D_y .

An apparent reversibility of the solid state redox reaction depends on the difference between the heterogeneous charge transfer on the particle |electrode interface and homogeneous charge transfers in the particle. The homogeneous exchange reaction of Eq. 10 plays the same role in the solid as the mass transfer in the solution. So, if the charge transfer over the particle| electrode interface is slower than the propagation of charges in the particle, the redox reaction appears irreversible.

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