

ORIGINAL PAPER

M. Lovrić · F. Scholz

A model for the propagation of a redox reaction through microcrystals

Received: 28 December 1996 / Accepted: 17 February 1997

Abstract Chronoamperometry of reversible redox reactions with the insertion of cations into solid particles immobilised at an electrode surface is analysed theoretically using a semiinfinite planar diffusion model. A coupled diffusion of electrons and ions within the crystal lattice is separated in two differential equations. The redox reaction is initiated by the polarisation of the three-phase boundary, where the crystal is in contact with both the electrode and the solution. From this contact line the redox reaction advances on the surface and into the crystal body by the diffusion of ions and conductance of electrons. The effects of the geometry and conductivity of the particles on the current are discussed.

Key words Chronoamperometry · Simulation · Solid state electrochemistry

Introduction

Abrasive stripping voltammetry is a new electroanalytical technique for the study of the electrochemical properties of solid materials [1–3]. It is based upon a preliminary mechanical transfer of trace amounts of a solid sample onto the surface of an electrode. The surface which is contaminated by traces of a powder can be used directly as a modified working electrode in voltammetric measurements. Many microcrystalline particles immobilised at the electrode surface exhibit mixed ionic and electronic transport [4–6]. Electroactive components of solid compounds can be reduced or

oxidised if the transfer of electrons is simultaneously followed by the insertion or expulsion of ions. The transport of electrons and that of ions through solid particles are coupled and proceed at the same rate because of electroneutrality [7]. The fastest species move ahead and generate an electric field in such a way that the faster species are slowed down and the slower ones are accelerated. At the surface of particles the ions are exchanged with the solution, and from there they may advance into the body of microcrystals. The electrons are supplied from the contacts of the particle with the electrode surface. The fluxes of both electrons and ions are caused by the gradient of the electrochemical potential in the solid compound. These fluxes obey Fick's laws of diffusion [7]. It was previously demonstrated that the Nernstian equilibrium was first established at the three-phase boundary, where the particle, the solution and the electrode are in contact [8]. This boundary is a line which surrounds the contact plane between the microcrystal and the electrode surface. From this line the redox reaction may advance along the surface and into the body of the particle. In this paper, a simple model of such insertion reactions is developed. It has been shown in experimental studies that some reactions are initially surface confined [12, 13], whereas others advance throughout the crystal from the very beginning [14]. The locus of the electrochemical reaction is always the double layer between the electrode (e.g. graphite) and the solid particle. The starting line of the electrochemical reaction is where the three phases, viz. electrode, solid compound and electrolyte solution, meet each other.

M. Lovrić (✉)
Centre for Marine Research, "Ruder Bošković" Institute,
POB 1016, 10000 Zagreb, Croatia
e-mail: slovric@olimp.irb.hr

F. Scholz
Institut für Chemie, Humboldt-Universität,
Hessische Str. 1-2, 10115 Berlin, Germany
e-mail: fritz=scholz@chemie.hu-berlin.de

Theory and discussion

A redox reaction with the insertion of cation C^+ is considered:



(Species enclosed by braces are confined to the solid state and species enclosed by square brackets are present in the electrolyte solution.)

It is assumed that the Nernst equilibrium is established at the three-phase boundary:

$$a_{\{C_m AX\}} \cdot a_{[C^+],x=0}^n = a_{\{C_{m+n} BX\}} \exp[nF(E - E^0)/RT] \quad (1)$$

where E is the electrode potential and E^0 is a standard potential of the redox reaction (I). E^0 depends on the electrolyte concentration according to the following equation [9]:

$$E^0 = E_{A/B}^0 + (RT/nF) \ln(K) \quad (2)$$

where $E_{A/B}^0$ is a standard potential of the partial redox reaction $\{C_m AX\} + ne^- \rightleftharpoons \{C_m BX\}^{n-}$, and K is an equilibrium constant of the ion-transfer reaction: $\{C_m BX\}^{n-} + n[C^+] \rightleftharpoons \{C_{m+n} BX\}$. The activities of the oxidized ($a_{\{C_m AX\}}$) and the reduced ($a_{\{C_{m+n} BX\}}$) forms of the solid compound are proportional to their mole fractions in the mixed crystal which is formed by the redox reaction [8]. If the densities of these two forms are not significantly different, the formal concentration of the ions A and B are related to their activities as $c_A = \rho_d \cdot a_{\{C_m AX\}}$ and $c_B = \rho_d \cdot a_{\{C_{m+n} BX\}}$, where ρ_d is a common density in mol/cm³. A diffusion of ions in the crystal is usually much slower than in the solution. In concentrated electrolytes it is safe to assume that the activity of dissolved ions at the surface of the particle is the same as in the bulk of the solution ($a_{[C^+],x=0} = a_{[C^+],\infty}$). So, the formal potential of the redox reaction (I) can be defined as:

$$E_f = E^0 + (RT/F) \ln a_{[C^+],\infty} \quad (3)$$

Some insertion compounds are electron conductors, but many are insulators [7]. If a certain redox-active insulator can exchange ions with the electrolyte, it can conduct electrons by a series of faradaic reactions between the neighbouring redox sites [10, 11]. It is shown in the Appendix that such faradaic conductivity obeys Fick's laws of diffusion.

The simplest approach to the problem of the coupled transport of electrons and ions is to imagine an infinite crystal attached to an infinite electrode surface. The coordinate system is situated as shown in Fig.1. The axis z coincides with the three-phase boundary between the electrode, the crystal and the solution. The electrode surface is located in the x - z plane, and its body occupies the semi-space $y < 0$. The remaining space ($y > 0$) is divided between the crystal ($x > 0$) and the solution ($x < 0$). The semi-axis $y > 0$ lies in the crystal surface facing the solution, and the semi-axis $x > 0$ is placed in the contact semi-plane between the crystal and the electrode.

It is assumed that the Nernst equilibrium is initially established along the axis z , where both electrons and ions are immediately available. Then the current is conducted over the crystal surface which is facing the

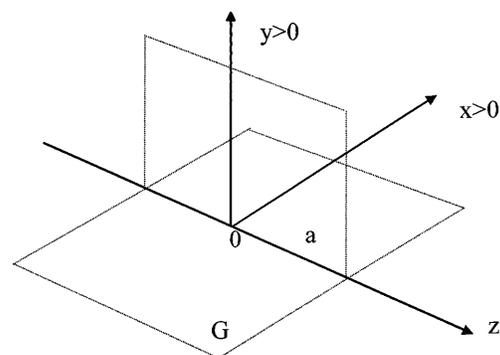


Fig. 1 Coordinate system with a part of the crystal/solution interface (a) and a part of the graphite surface (G)

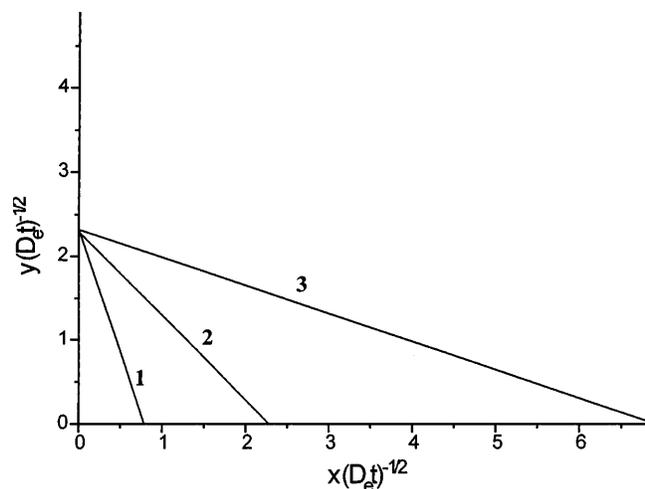


Fig. 2 Isoconcentration lines $c_B = c_{B,x=0,y=0}/10$ in the dimensionless volume of the solid particle for $D_e = 9D_c$ (1), $D_e = D_c$ (2) and $D_e = D_c/9$ (3)

solution by the diffusion of electrons, because the ions from the solution can readily compensate 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. The fluxes of electrons and ions inside the solid particle are mutually perpendicular.

The surface diffusion of electrons is described by the differential equation:

$$\partial \Gamma_B / \partial t = D_e (\partial^2 \Gamma_B / \partial y^2) \quad (4)$$

with the initial and boundary conditions:

$$t = 0, \quad y \geq 0 : \Gamma_B = 0, \quad \Gamma_A = \Gamma \quad (5)$$

$$t > 0, \quad y \rightarrow \infty : \Gamma_B \rightarrow 0, \quad \Gamma_A \rightarrow \Gamma \quad (6)$$

$$y \geq 0 : \Gamma_A + \Gamma_B = \Gamma \quad (7)$$

$$y = 0 : \Gamma_{A,y=0} = \Gamma_{B,y=0} \exp(\varphi) \quad (8)$$

$$\varphi = nF(E - E_f) / RT \quad (9)$$

$$D_e (d\Gamma_B / dy)_{y=0} = -i_s / nFb \quad (10)$$

where Γ_A and Γ_B are formal surface concentrations of ions A and B, and Γ is their common surface density in mol/cm². It is related to the volume density by the ratio $\Gamma/\rho_d = 10^{-8}$ cm. D_e is a diffusion coefficient for electrons, i_s is a surface component of the current, and b is a length of the line of contact between the electrode, the crystal and the solution. It is assumed that $b \gg (\pi D_e t)^{1/2}$, for any t , so that the edge effects can be neglected.

Under chronoamperometric conditions (i.e., at a constant electrode potential E), the solutions of Eqs. 4–10 are:

$$\Gamma_B = \Gamma[1 + \exp(\varphi)]^{-1} \operatorname{erfc}\left[y(D_e t)^{-1/2}/2\right] \quad (11)$$

$$i_s = nFb\Gamma[1 + \exp(\varphi)]^{-1}(D_e/\pi t)^{1/2} \quad (12)$$

Within the solid particle, the diffusions of electrons and ions are coupled. The advance of electrons is slower than at the surface because they must wait for ions, and the ions cannot diffuse in the direction of the y -axis because they cannot move in front of the electrons. So, the diffusion of ions is described by the differential equation:

$$\partial c_B/\partial t = D_c(\partial^2 c_B/\partial x^2) \quad (13)$$

with the initial and boundary conditions:

$$t = 0, x \geq 0 : c_B = 0, c_A = \rho_d \quad (14)$$

$$t > 0, x \rightarrow \infty : c_B \rightarrow 0, c_A \rightarrow \rho_d \quad (15)$$

$$x \geq 0 : c_A + c_B = \rho_d \quad (16)$$

$$y = 0, x = 0 : (c_A)_{x=0,y=0} = (c_B)_{x=0,y=0} \exp(\varphi) \quad (17)$$

$$x = 0 : (c_B)_{x=0} = \rho_d[1 + \exp(\varphi)]^{-1} \quad (18)$$

$$\operatorname{erfc}\left[y(D_e t)^{-1/2}/2\right] \quad (18)$$

$$nFD_c(\partial c_B/\partial x)_{x=0} = -di_c/dS \quad (19)$$

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

where D_c is a diffusion coefficient for ions, i_c is a volume component of the current, and $S = b \cdot y$ is an area of the crystal surface which is exposed to the solution. In this model S is infinite. Under chronoamperometric conditions, the solutions of Eqs. 13–20 are:

$$c_B = \rho_d[1 + \exp(\varphi)]^{-1} \operatorname{erfc}\left\{\left[x(D_e t)^{-1/2}/2\right] + \left[y(D_e t)^{-1/2}/2\right]\right\} \quad (21)$$

$$di_c/dS = nFD_c^{1/2}\rho_d[1 + \exp(\varphi)]^{-1}(\pi t)^{-1/2} \exp(-y^2/4D_e t) \quad (22)$$

Eq. 21 shows that the product of the redox reaction (I) appears primarily near the two crystal surfaces: the one which faces the solution ($x = 0$) and the one which is in contact with the electrode ($y = 0$). In both planes, the concentration of the product decreases with the distance from the three-phase boundary. A distribution of the product in a real, finite microcrystal depends on the ratio between diffusion coefficient of ions and electrons. If electrons move quickly along the surface and the ions

are slow, the film of the product is formed at the outer surface and grows inward. In the opposite case, the film is formed at the electrode surface and grows outward. An example of three possible concentration profiles of the product is shown in Fig. 2.

The potential inside the crystal can be calculated by introducing Eqs. 16 and 21 into the Nernst equation:

$$E_{x,y} = E_f + (RT/nF) \ln[(c_A)_{x,y}/(c_B)_{x,y}] \quad (23)$$

$$E_{x,y} = E_f + (RT/nF) \ln \left\{ \exp[nF(E_{x=0,y=0} - E_f)/RT] \cdot \operatorname{erf}\left[\left(x(D_e t)^{-1/2}/2\right) + \left(y(D_e t)^{-1/2}/2\right)\right] \right\} - (RT/nF) \ln \left\{ \operatorname{erfc}\left[\left(x(D_e t)^{-1/2}/2\right) + \left(y(D_e t)^{-1/2}/2\right)\right] \right\} \quad (24)$$

Since $\lim_{t \rightarrow \infty} E_{x,y} = E_{x=0,y=0}$, the whole crystal acquires the electrode potential when the redox reaction (I) is completed.

Equation 22 indicates that the current density is the highest at the contact line b , where $y = 0$, and decreases along the crystal surface. The current is obtained by integrating Eq. (22) over the whole surface area:

$$i_c = nFb\rho_d(D_c/\pi t)^{1/2}[1 + \exp(\varphi)]^{-1} \int_0^\infty \exp(-y^2/4D_e t) dy \quad (25)$$

The integral in Eq. 25 is equal to $(\pi D_e t)^{1/2}$, so that the volume component of the current is:

$$i_c = nFb\rho_d(D_c D_e)^{1/2}[1 + \exp(\varphi)]^{-1} \quad (26)$$

This is a steady-state current because of the assumption that the crystal has an infinite volume, i.e. it is only a consequence of the geometry and does not depend on the particular transport properties of ions and electrons. Finite crystals can be electrolysed exhaustively, and thus they would give rise to time-dependent currents. Here, it is important to notice that the total current consists of the volume and the surface components:

$$i = nFb\rho_d D_e^{1/2}[1 + \exp(\varphi)]^{-1} \left[D_c^{1/2} + 10^{-8}(\pi t)^{-1/2} \right] \quad (27)$$

Generally, the surface component can be neglected, but there are systems in which only this component can be recorded. The reduction of many organic substances is followed by the protonisation of the product (e.g. the quinone-hydro-quinone couple). When their solid particles are mechanically attached to the electrode and polarised, the molecules at the surface of microcrystals can be reduced and protonised by the faradaic conductivity, but protons may not be able to penetrate below this monolayer. So, the volume component of the current does not exist.

For cyclic voltammetry, the solutions of Eqs. 4–10 and Eqs. 13–20 are:

$$\int_0^t i_s(t-\tau)^{-1/2} d\tau = nFb\Gamma(\pi D_c)^{1/2} [1 + \exp(\varphi_{st} + at)]^{-1} \quad (28)$$

$$i_c = nFb\rho_d(D_c D_e)^{1/2} [1 + \exp(\varphi_{st} + at)]^{-1} \quad (29)$$

where $\varphi_{st} = nF(E_{st} - E_r)/RT$, $a = nFv/RT$, $v = dE/dt$ and E_{st} is a starting electrode potential.

Eq. 29 is a formula of the polarographic wave, which is in agreement with the steady-state conditions in the assumed infinite crystal.

The finite volume of the crystal can be simulated by restricting the diffusion in one or both directions. A simpler case is the restricted diffusion along the x axis. This corresponds to an infinite crystal membrane with the thickness $2x_0$. To calculate the volume component of the current, the condition:

$$x = x_0 : (\partial c_B / \partial x)_{x=x_0} = 0 \quad (30)$$

must be used instead of Eq. 15. The solution of Eqs. 13, 14, 16–20 and Eq. 30 for chronoamperometry is:

$$i_c = 2nFb\rho_d(D_c D_e)^{1/2} [1 + \exp(\varphi)]^{-1} \left\{ 1 + 2 \sum_{m=1}^{\infty} (-1)^m \operatorname{erfc} \left[mx_0 (D_c t)^{-1/2} \right] \right\} \quad (31)$$

The factor 2 appears because the membrane has two surfaces.

To restrict the diffusion in both x and y directions, the conditions:

$$y = y_0 : (d\Gamma_B / dy)_{y=y_0} = 0 \quad (32)$$

together with Eq. 30 apply instead of Eqs. 6 and 15. After the integration of current density between $y = 0$ and $y = y_0$, the solution of Eqs. 4 and 13 is a volume component of the current which passes through the single, restricted crystal surface. For constant potential, it is:

$$\begin{aligned} i_c = nFb\rho_d(D_c D_e)^{1/2} [1 + \exp(\varphi)]^{-1} & \left\{ \operatorname{erf}[y_0 (D_e t)^{-1/2} / 2] \right. \\ & + 2 \sum_{p=1}^{\infty} (-1)^p \left[\operatorname{erf} \left(px_0 (D_c t)^{-1/2} + y_0 (D_e t)^{-1/2} / 2 \right) \right. \\ & \left. \left. - \operatorname{erf} \left(px_0 (D_c t)^{-1/2} \right) \right] \right. \\ & + \sum_{m=1}^{\infty} (-1)^m \left[\operatorname{erf} \left((m+1/2)y_0 (D_e t)^{-1/2} \right) \right. \\ & \left. + \operatorname{erf} \left((m-1/2)y_0 (D_e t)^{-1/2} \right) - 2 \operatorname{erf} \left(my_0 (D_e t)^{-1/2} \right) \right] \\ & + 2 \sum_{p=1}^{\infty} \sum_{m=1}^{\infty} (-1)^{p+m} \left[\operatorname{erf} \left(px_0 (D_c t)^{-1/2} + (m+1/2)y_0 \right. \right. \\ & \left. \left. \times (D_e t)^{-1/2} \right) + \operatorname{erf} \left(px_0 (D_c t)^{-1/2} + (m-1/2) \right. \right. \end{aligned}$$

$$\left. \left. \times y_0 (D_e t)^{-1/2} \right) - 2 \operatorname{erf} \left(px_0 (D_c t)^{-1/2} + my_0 (D_e t)^{-1/2} \right) \right] \left. \right\} \quad (33)$$

This result applies to hypothetical conditions which are not entirely realistic, but it shows the general influence of the finite volume on the calculation of currents. It is most probable that for real microcrystals the solutions can be obtained only by numerical simulation. It is not a purpose of our paper to pursue this further, but merely to establish the general approach to the problem. However, it is obvious that the specific response of a particular microcrystal depends on its geometry. So, the current in abrasive stripping voltammetry is an average response of many different geometric forms of microcrystals.

Finally, the redox reactions of conductive insertion compounds can be briefly investigated using the same model of an infinite crystal. At the surface of a conductive solid particle, the current obeys Ohm's law: $i = U/R$, where $U_y = (E_y) - E_{y=0}$. The resistance R increases with the distance from the electrode surface: $R = \rho_R y$, where ρ_R is a specific resistance. A charge which is needed to reduce a certain area S_r of the surface is equal to $Q = nF\Gamma_B S_r$, and the current needed to expand this area is $i = nFbd(\Gamma_B y_r)/dt$, because $S_r = by_r$. The surface concentration Γ_B is defined by Eqs. 5–8. As the first approximation, it can be assumed that the potential of the whole area S_r is equal to the electrode potential, so that $d\Gamma_B/dt = 0$ inside the area and $\Gamma_B = \Gamma [1 + \exp(\varphi)]^{-1}$. Outside this area $\Gamma_B = 0$. This is a concept of the advancing front. It enables the calculation of the surface current by solving the simple differential equation:

$$nFb\Gamma [1 + \exp(\varphi)]^{-1} dy/dt = U / \rho_R y \quad (34)$$

$$\text{The solution is: } y_r = k_y t^{1/2} \quad (35)$$

$$\text{where: } k_y = [2U(1 + \exp(\varphi)) / nFb\Gamma\rho_R]^{1/2}$$

$$\text{Hence: } S_r = bk_y t^{1/2} \quad (36)$$

$$\text{and: } i_s = U\rho_R^{-1} k_y^{-1} t^{-1/2} \quad (37)$$

The surface component of the current decreases with the square root of time, as it does in the electron diffusion model (see Eq. 12).

A gradient of electrochemical potential is created in that part of the crystal which is covered by the reduced area S_r . The ions enter the lattice only through S_r and diffuse parallel to the electrode surface. The perpendicular component of the electrochemical potential gradient causes the movement of electrons from the electrode into the lattice. So, the density of the volume component of the current is equal throughout the reduced area S_r . This current can be calculated by solving the differential equation (Eq. 13), together with Eqs. 14–17, 19, 20 and a new boundary condition:

$$x = 0 : (c_B)_{x=0} = [1 + \exp(\varphi)]^{-1} \rho_d \quad (38)$$

The solution is:

$$i_c/S_r = nF\rho_d(D_c/\pi t)^{1/2}[1 + \exp(\varphi)]^{-1} \quad (39)$$

Hence:

$$i_c = nFb\rho_d(D_c/\pi)^{1/2}k_y[1 + \exp(\varphi)]^{-1} \quad (40)$$

The solution is again a steady-state current because of the assumed infinite volume of the crystal.

The concept of the advancing front is only a rough approximation in which a continuous change of the potential on the crystal surface and the accompanying distribution of surface concentrations of ions B are neglected. However, it can be useful for the calculation of redox reactions with the insertion in solid, conductive particles with large volume and small surface area, such as a hemisphere. If electrons are conducted over the finite surface very quickly, we can assume that the potential of the whole surface becomes equal to the electrode potential at the very beginning of the experiment, even before the ions start to diffuse into the lattice. This means that the surface component of faradaic current behaves like a capacitive current: in the chronoamperometric measurement they are usually both neglected. This assumption simplifies the boundary conditions for the diffusion of ions because it implies that the concentration of ions B at the surface does not depend on the distance from the three-phase boundary. The volume component of faradaic current in the hemispherical particle with the radius r_0 can be calculated by solving the following equations:

$$\partial(rc_B)/\partial t = D_c[\partial^2(rc_B)/\partial r^2] \quad (41)$$

$$t = 0, 0 \leq r \leq r_0 : c_B = 0, c_A = \rho_d \quad (42)$$

$$t > 0, r = r_0 : (c_B)_{r=r_0} = \rho_d[1 + \exp(\varphi)]^{-1} \quad (43)$$

Equation 41 is the condensed form of the well known equation

$$\frac{\partial c_B}{\partial t} = Dr^{-2}\partial(r^2\partial c_B/\partial r)/\partial r. \quad (44)$$

$$S = 2r_0^2\pi \quad (45)$$

The solutions are:

$$i_c = nF\rho_d[1 + \exp(\varphi)]^{-1} \left\{ 2r_0^2(\pi D_c/t)^{1/2} \times \left[1 + 2 \sum_{p=1}^{\infty} \exp(-p^2 r_0^2/tD_c) \right] - 2r_0\pi D_c \right\} \quad (46)$$

$$c_B = \rho_d[1 + \exp(\varphi)]^{-1}(r_0/r) \left\{ \operatorname{erfc}[(r + r_0)(D_c t)^{-1/2}/2] - \operatorname{erfc}[(r_0 - r)(D_c t)^{-1/2}/2] \right\}$$

$$+ \sum_{p=1}^{\infty} \operatorname{erfc} \left[((2p+1)r_0 + r)(D_c t)^{-1/2}/2 \right] - \sum_{p=1}^{\infty} \operatorname{erfc} \left[((2p+1)r_0 - r)(D_c t)^{-1/2}/2 \right] \quad (47)$$

This result can be used to analyse the response in abrasive stripping voltammetry of conductive solid compounds if a certain statistical distribution of radii of particles is applied. However, by this approximation the specific geometric forms of various microcrystals are entirely neglected. So, the application of Eqs. 46 and 47 may appear rather limited.

Conclusions

With an increasing number of studies devoted to the voltammetric behaviour of microparticles, it becomes more and more important to attain a detailed understanding of the underlying principles of charge and ion propagation during the electrochemical reactions. Experimental studies have shown that some reactions are initially surface confined and only later proceed as a volume reaction [12, 13], whereas others, from the very beginning, advance throughout the crystals [14]. A theoretical treatment of the very simple model of the three-phase boundary which exists when a crystal is attached to a solid electrode surface allows the following conclusions: (a) The three-phase boundary is always the starting line for the reaction front, independently of the geometry of the particle and its conductivity. (b) The reaction will be surface confined when the diffusion of ions into the bulk of the crystal is impossible or very slow. (c) Generally, the net current is the sum of a surface current and a bulk current. (d) In the case that both the surface and the bulk reaction proceed at comparable rates, the reaction front expands from the three-phase boundary as a space with exponential borderlines in the x and y directions. (v) The surface current will be negligible in cases where the bulk reaction is dominating.

In the theory of these redox reactions, the mass transfer must be calculated by a three-dimensional diffusion model, which can be reduced to the two-dimensional model in the case of favourable symmetry of the system. This is because in principle the concentrations of the redox species on the surface of the particle are functions of the time and the distance from the three-phase boundary. This condition applies to both electron conductors and insulators possessing faradaic conductivity. However, if the electron conductivity of the solid particle is very high and its surface area is relatively small, the approximation of the quickly advancing front may be used, which simplifies the calculations significantly. This approximation is based on the assumption of a uniform distribution of redox species on the surface of the particle as an initial condition for the differential

equation describing the diffusion of ions through the particle. It was previously applied to thin solid film electrodes [15, 16] and in this paper to small hemispherical particles. However, its application is restricted to very good electron-conducting materials.

Thermodynamic and kinetic analyses indicate that redox-active insulators can transfer electrons by a series of electron exchange reactions. However, if this faradaic conductivity is very low, the total current will also be rather small, regardless of the mobility of ions in the solid, because the theory shows that the conductance of electrons is essential for the overall chronoamperometric and voltammetric responses.

Appendix

If a redox reaction



is in equilibrium, an exchange reaction



$$k c_A c_B = k c_B c_A \quad (\text{A3})$$

can be formulated by analogy to the exchange reaction which exists in the equilibrium of two redox couples. In the mixed crystal which consists of nonmetallic redox components A and B, the change of the concentration of the component B at a certain position x depends on the difference in rates of its exchange reactions with the neighbouring components A.

$$d(c_B)_x/dt = k(c_B)_{x-dx}(c_A)_x + k(c_A)_x(c_B)_{x+dx} - k(c_A)_{x-dx}(c_B)_x - k(c_A)_{x+dx}(c_B)_x \quad (\text{A4})$$

By assuming that

$$(c_B)_{x+dx} = (c_B)_x + (\partial c_B/\partial x)_{x+dx} dx \quad (\text{A5})$$

$$(c_B)_{x-dx} = (c_B)_x - (\partial c_B/\partial x)_{x-dx} dx \quad (\text{A6})$$

$$(c_A)_x + (c_B)_x = \rho_d \quad (\text{A7})$$

one obtains

$$d(c_B)_x/dt = k\rho_d dx [(\partial c_B/\partial x)_{x+dx} - (\partial c_B/\partial x)_{x-dx}] \quad (\text{A8})$$

where

$$(\partial c_B/\partial x)_{x+dx} - (\partial c_B/\partial x)_{x-dx} = d(\partial c_B/\partial x) \quad (\text{A9})$$

and

$$d(\partial c_B/\partial x) = dx(\partial^2 c_B/\partial x^2) \quad (\text{A10})$$

So

$$dc_B/dt = k\rho_d(dx)^2(\partial^2 c_B/\partial x^2) \quad (\text{A11})$$

The product $k\rho_d(dx)^2$ has dimensions of a diffusion coefficient (cm^2/s). A differential dx corresponds to a distance between two layers of atoms in the crystal.

A net flux of electrons is equal to the product of the difference between the rates of the exchange reactions and the distance between the reacting redox components:

$$j_e - (v_f - v_b)dx \quad (\text{A12})$$

$$j_e = \{k(c_B)_{x-dx}(c_A)_x - k(c_A)_{x-dx}(c_B)_x\}dx \quad (\text{A13})$$

Using Eqs. A6 and A7, one obtains

$$j_e = -k\rho_d(dx)^2(\partial c_B/\partial x)_{x-dx} \quad (\text{A14})$$

This flux is caused by the gradients of electrochemical potentials in the solid particle. As the components A and B cannot diffuse, the electrons are transferred by exchange reactions.

Acknowledgements We acknowledge support by the respective Ministries of Science in the framework of a bilateral German-Croatian research program and by Fonds der Chemischen Industrie.

References

- Scholz F, Nitschke L, Henrion G (1989) *Fresenius J Anal Chem* 334: 56
- Scholz F, Lange B (1992) *Trends Anal Chem* 11: 359
- Scholz F, Meyer B (1994) *Chem Soc Rev*: 341
- Dostal A, Meyer B, Scholz F, Schröder U, Bond AM, Marken F, Shaw SJ (1995) *J Phys Chem* 99: 2096
- Dostal A, Schröder U, Scholz F (1995) *Inorg Chem* 34: 1711
- Komorsky-Lovrić Š (1995) *J Electroanal Chem* 397: 211
- Weppner W (1995) In: Bruce PG (ed) *Solid state electrochemistry*. Cambridge University Press, Cambridge, pp 199–228
- Jaworsky A, Stojek Z, Scholz F (1993) *J Electroanal Chem* 354: 1
- Scholz F, Dostal A (1995) *Angew Chem* 107: 2876
- Ksenzhek OS, Barsukov VZ, Matveyev VV (1977) *Dokl. Akad. Nauk USSR* 132: 1120
- Barsukov VZ, Matveyev VV (1983) *Elektrokhimiya* 19: 1110
- Bond AM, Cooper JB, Marken F, Way DM (1995) *J Electroanal Chem* 396: 407
- Bond AM, Marken F (1994) *J Electroanal Chem* 372: 125
- Dostal A, Hermes M, Scholz F (1996) *J Electroanal Chem* 415: 133
- Barral G, Diard JP, Montella C (1985) *Electrochim Acta* 30: 585
- Lovrić M, Komorsky-Lovrić Š, Scholz F (1997) *Electroanalysis* 9 (in press)