

Full Paper

Simulation of Influence of Variable Diffusion Coefficient in Cyclic Voltammetry

Milivoj Lovrić* and Šebojka Komorsky-Lovrić

Department of marine and environmental research, “Ruđer Bošković” Institute, 10000 Zagreb, Hrvatska (Croatia)

* Corresponding Author, Tel.: +3851 456 1046

E-Mail: mlovric@irb.hr

Received: 14 November 2014 / Received in revised form: 12 April 2015 /

Accepted: 16 April 2015 / Published online: 30 April 2015

Abstract- A model of electrode reaction of solid compound that includes an insertion of cations from the solution is developed and the influence of concentration-dependent diffusion coefficient in cyclic voltammetry is investigated theoretically. Generally, the form of response does not change significantly, but in some cases the cathodic peak may split in two.

Keywords- Cyclic voltammetry, Diffusion coefficient, Solid-state electrode reactions, Insertion compounds

1. INTRODUCTION

Mass transport by molecular diffusion is one of the basic mechanisms in many branches of chemistry [1-3]. In solutions and gases the diffusion coefficients are constants, but there are many systems in which the transport of material can be explained by the concentration-dependent diffusion coefficient [4-8]. Some examples are diffusion of phosphorus in germanium [9], nitrogen in expanded austenite [10], protons in silica sol-gel glasses [11], methylene chloride in polystyrene [12], butylferrocene in liquid crystals [13] and polystyrene in toluene and cyclohexane [14]. Furthermore, this effect was observed in the transport of gas into the heavy oil [15], the diffusion of impurity into metals and semiconductors at high

temperatures [16], the water movement in legumes [17] and in alkali metal chloride electrolytes [18] and in self-diffusion of globular proteins in water [19,20]. The charging and discharging of the solid-solution type of insertion electrodes result in monotonous concentration profiles of guest ions in the electrode bulk [21,22], but highly attractive short-range interactions between the host and guest ions may cause the formation of separate phases with different concentrations of guest ions [23-26]. At the boundary between the coexisting phases the diffusion coefficient of ions and electrons depends on the concentration of guest ions [23,24]. In this communication the influence of variable diffusion coefficient is analyzed theoretically for cyclic voltammetry of insertion compound

2. THE MODEL

A reversible reduction of a certain solid compound, accompanied by the insertion of a cation C^+ from the solution into the particle, is considered:



The species in braces are confined to the solid phase. The activities of redox components of the solid compound are assumed to be proportional to their molar fractions in the mixed crystal. It is also assumed that a small cylinder of the insertion compound is pressed into an electrode surface in such a way that only one of its surfaces is exposed to the solution (see Scheme 1). The compound is a good electronic conductor and its surface, which is in contact with the solution, acquires the electrode potential at the very beginning of the experiment. Cations can diffuse through this surface along the longitudinal axis x of the cylinder. So, the mass transfer can be described by the planar diffusion model [1]:

$$\partial c / \partial t = D(\partial^2 c / \partial x^2) + (\partial D / \partial c)(\partial c / \partial x)^2 \quad (2)$$

Here, c is the molar concentration of the reduced component $\{Cred\}$. The starting and the boundary conditions are the following:

$$t = 0, x \geq 0 : \quad c = 0 \quad (3)$$

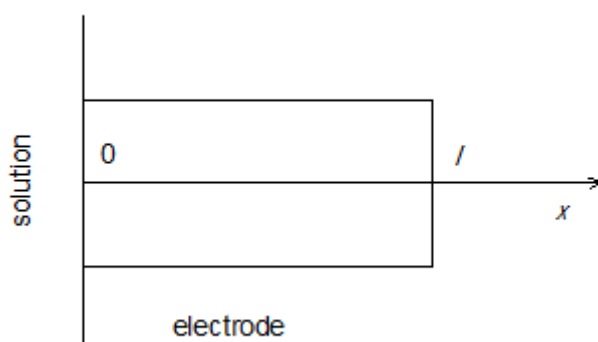
$$t > 0, x = 0 : \quad c = \rho / (1 + \exp(\varphi)) \quad (4)$$

$$\partial c / \partial x = I / FSD \quad (5)$$

$$x = l : \quad \partial c / \partial x = 0 \quad (6)$$

Here, ρ is a density of the solid compound in mol/cm^3 , $\varphi = F(E - E_f) / RT$ is a dimensionless electrode potential, E_f is a formal potential of the redox reaction (1), S is the area of the solid particle surface that is exposed to the solution, D is the concentration-dependent diffusion coefficient of ions C^+ in the crystal lattice, l is the thickness of the cylinder and I is a current. Equation (2) is solved by the finite difference method [27]. The

dimensionless current $\Phi = I(FS\rho)^{-1}(DFv/RT)^{-1/2}$, where v is a scan rate, is calculated as a function of the electrode potential.



Scheme 1. A scheme of the solid electroactive microcylinder pressed into the working electrode surface

3. RESULTS AND DISCUSSION

In the first calculations it was assumed that the diffusion coefficient depended linearly on the concentration of the reduced component:

$$D(c) = D(k + (1 - k) c/\rho) \quad (7)$$

$$\partial D(c)/\partial c = D(1 - k) / \rho \quad (8)$$

The parameter k defines the slope of this linear relationship. If $k=1$ the diffusion coefficient is independent of concentration, while for $k=0$ the value of $D(c)$ changes from zero, for $c=0$, to D for $c = \rho$. Figure 1 shows that under the influence of variable diffusion coefficient the peak currents of cyclic voltammogram are smaller and the difference between peak potentials is bigger than in the case of constant diffusion coefficient. The curve (1) corresponds to $k=0.15$. It is characterized by the following extremes: $\Phi_{\min}=-0.3554$, $E_{\min}-E_f=-0.0386$ V, $\Phi_{\max}=0.2443$, $E_{\max}-E_f=0.0244$ V and $E_{\max}-E_{\min}=63$ mV. The curve (2) in this figure serves for the control. Its extremes are the following: $\Phi_{\min} = -0.4463$, $E_{\min}-E_f=-0.0285$ V, $\Phi_{\max}=0.3076$, $E_{\max}-E_f=0.0297$ V and $E_{\max} - E_{\min} = 58.2$ mV. These differences are caused by the thinner diffusion layer corresponding to the diminished diffusion coefficient. This is shown in Figure 2. If $k = 1$ the concentration profile is a concave curve, with the highest derivative at $x \rightarrow 0$, but if $k=0$ the profile is a convex curve for $x/\Delta x < 40$ and its derivative is the smallest at $x \rightarrow 0$. This is because the diffusion coefficient is lesser as the concentration is decreased and the product of reaction (1) remains near the electrode surface instead of being carried out into solution by the diffusion.

Figure 3 shows the influence of the parameter k on the peak currents and peak potentials of cyclic voltammograms. These relationships can be approximated by the following equations: $\Phi_{\min} = -0.1057 \times k - 0.3406$, $\Phi_{\max} = 0.0745 \times k + 0.2331$, $E_{\max} - E_f = 0.009 \times k + 0.021$ V, $E_{\min} - E_f = 0.011 \times k - 0.039$ V (for $0.3 < k \leq 1$) and $E_{\min} - E_f = 0.016 \times k - 0.041$ V (for $0 \leq k \leq 0.2$).

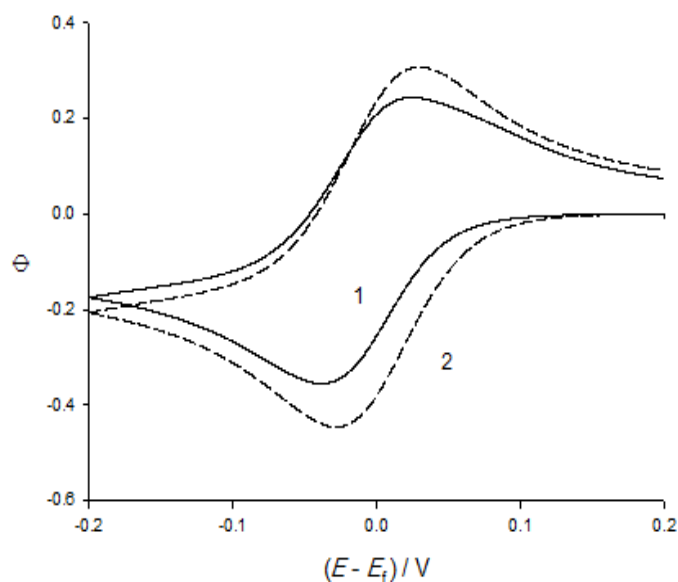


Fig. 1. Dimensionless cyclic voltammograms influenced by the concentration-dependent diffusion coefficient defined by eq. (7); $k = 0.15$ (1) and 1 (2)

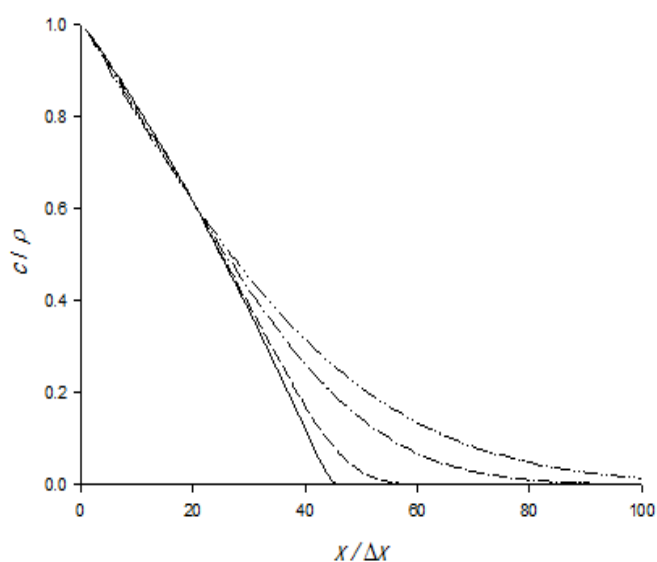
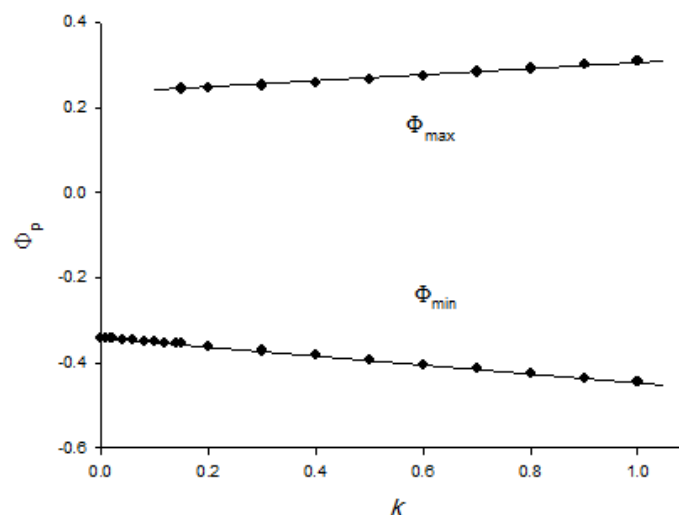
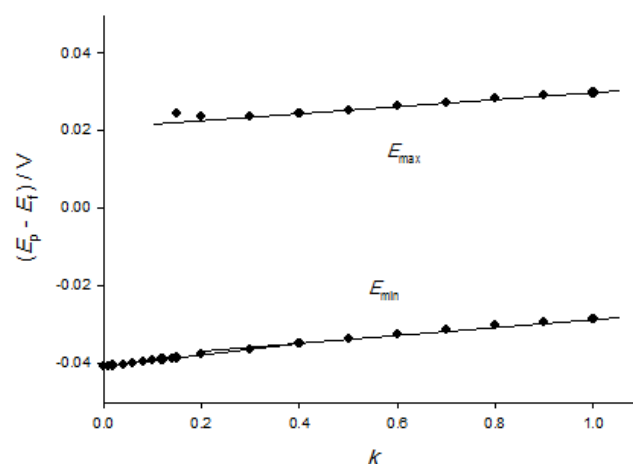


Fig. 2. Concentration profiles of the reduced component at -0.2 V vs. E_f . Diffusion coefficient is defined by eq. (7): $k = 0$ (—), 0.1 (---), 0.5 (- · - · -) and 1 (- · · - · -)



(A)



(B)

Fig. 3. Dependence of peak currents (A) and peak potentials (B) of cyclic voltammograms influenced by the concentration-dependent diffusion coefficient (eq. 7) on the parameter k . Straight lines are linear approximations

In the second set of calculations it was assumed that diffusion coefficient decreases with the increasing concentration:

$$D(c) = D(1 - kc/\rho) \tag{9}$$

$$\partial D(c)/\partial c = -kD/\rho \tag{10}$$

If $k < 0.8$ the peak currents and potentials depend linearly on this parameter: $\Phi_{\min} = 0.111 \times k - 0.4463$, $\Phi_{\max} = -0.084 \times k + 0.3076$, $E_{\min} - E_f = 0.0088 \times k - 0.0285$ V and $E_{\max} - E_f = 0.0083 \times k +$

0.0297 V. However, in the narrow range $0.84 \leq k \leq 0.8442$ the dimensionless minimum current decreases from -0.4356 to -0.6011 and the potential of minimum changes from -0.107 V to -0.152 V. This can be seen in Figure 4. The development of the new peak can be partly explained by the fact that the diffusion coefficient is the smallest at the electrode surface and increases through the diffusion layer. Figure 5 shows concentration profiles at -0.2 V vs. E_f for various values of the parameter k . If $k=0$ the diffusion coefficient is independent of the concentration of the product, while for $k=0.8$ the ratio $D(c) / D$ is smaller than 0.36 if $c/\rho > 0.8$. For this reason the space gradient of the concentration at the electrode surface is higher for $k=0.8$ than for $k=0$. At lower concentrations the diffusion layer expands faster and its thickness becomes concentration independent.

Finally, two parabolic relationships were considered:

$$D(c) = D \left(k + \frac{c}{\rho} - \left(\frac{c}{\rho} \right)^2 \right) \quad (11)$$

$$\partial D(c) / \partial (c/\rho) = D \left(1 - 2 \frac{c}{\rho} \right) \quad (12)$$

$$D(c) = D \left(k - \frac{c}{\rho} + \left(\frac{c}{\rho} \right)^2 \right) \quad (13)$$

$$\partial D(c) / \partial (c/\rho) = D \left(2 \frac{c}{\rho} - 1 \right) \quad (14)$$

Diffusion coefficient defined by eq. (11) starts from the minimum ($D_{\min}=kD$) for $c=0$, increases to the maximum ($D_{\max}=(k+0.25)D$) for $c/\rho=0.5$, and decreases back to D_{\min} for $c=\rho$. As long as $k>0$ the cyclic voltammogram exhibits a single minimum and a single maximum, as in Fig. 1.

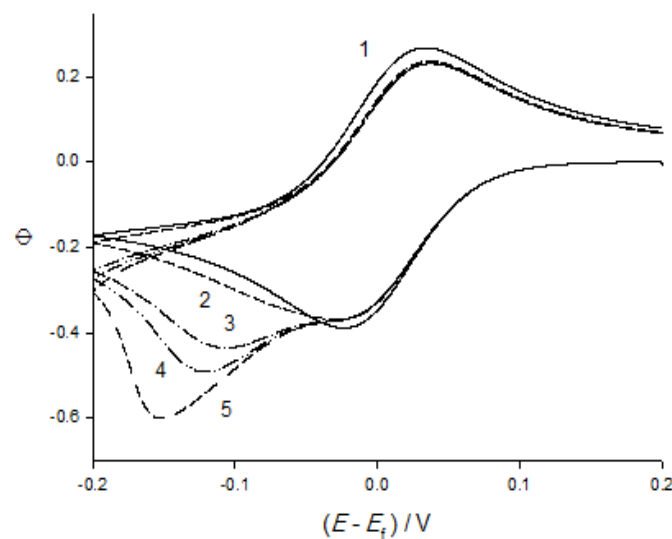


Fig. 4. Dimensionless cyclic voltammograms influenced by the concentration-dependent diffusion coefficient defined by eq. (9): $k=0.5$ (1), 0.8 (2), 0.84 (3), 0.843 (4) and 0.8442 (5)

If $k=0.75$ these extremes are the following: $\Phi_{\min}=-0.4359$, $E_{\min}-E_f = -0.0258$ V, $\Phi_{\max}=0.2969$ and $E_{\max}-E_f=0.0274$ V. The maximum diffusion coefficient cannot be smaller than $0.25 D$ and the values of extremes of cyclic voltammogram tend to constants as the parameter k tends to zero. These limiting values are the following: $\Phi_{\min}=-0.2043$, $E_{\min}-E_f = -0.0202$ V, $\Phi_{\max}=0.1338$ and $E_{\max}-E_f=0.0229$ V. They apply to $k \leq 10^{-3}$. However, our calculations do not apply to $k=0$.

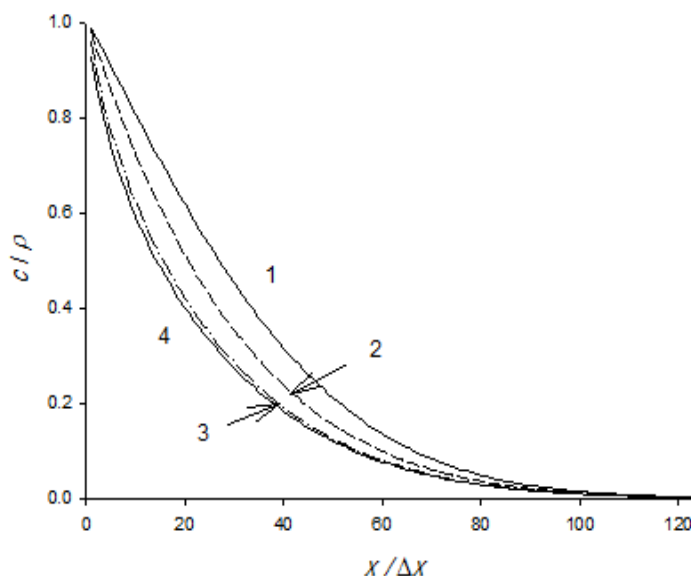


Fig. 5. Concentration profiles of the reduced component influenced by the diffusion coefficient defined by eq. (9). $E-E_f=-0.2$ V and $k=0$ (1), 0.5 (2), 0.8 (3) and 0.8442 (4)

In the case of diffusion coefficient that is defined by eq. (13), its value changes from the maximum ($D_{\max}=kD$), for $c=0$, to the minimum ($D_{\min}=(k-0.25)D$), for $c/\rho=0.5$, and back to the maximum for $c=\rho$. If $k=1$ the cyclic voltammogram is similar to the one shown in Fig. 1. Its characteristics are the following: $\Phi_{\min}=-0.3923$, $E_{\min}-E_f=-0.0311$ V, $\Phi_{\max}=0.2752$ and $E_{\max}-E_f=0.0322$ V. Within the range $1 > k \geq 0.5$ the response changes only quantitatively: absolute values of minima and maxima decrease as the parameter k is diminished and the potentials of minima and maxima change to -0.0409 V and 0.0403 V, respectively. Figure 6 shows that below $k=0.4$ a new peak “b” appears at $E_p-E_f = 0.000 \pm 0.003$ V. It is accompanied by the shoulder in the anodic branch of cyclic voltammogram. The cathodic peak “a” and its anodic counterpart do not change significantly within this range of the parameter k values. If $k=0.34$, the potentials of these peaks are -0.0572 V and 0.0504 V vs. E_f . The origin of the peak “b” could be connected to the minimum diffusion coefficient that corresponds to $c/\rho=0.5$. This dimensionless concentration appears at electrode surface if the

potential is equal to the formal potential. The current increases again as the concentration arises above $\rho/2$ at lower potentials.

Dependence of diffusion coefficient on the concentration of diffusing ions that is investigated in this paper is purely hypothetical and the consequences of the chosen relationships on cyclic voltammograms are only theoretical. However, these results may serve as possible explanation of similar experimental curves that may be observed in future. Variable diffusion coefficients may appear in the transport processes through membranes [6, 28]. Cyclic voltammetry is used for electrochemical characterization of intercalation mechanisms and diffusion processes in the insertion electrodes [29,30]. These electrodes are important for the development of chemical sensors [30-32].

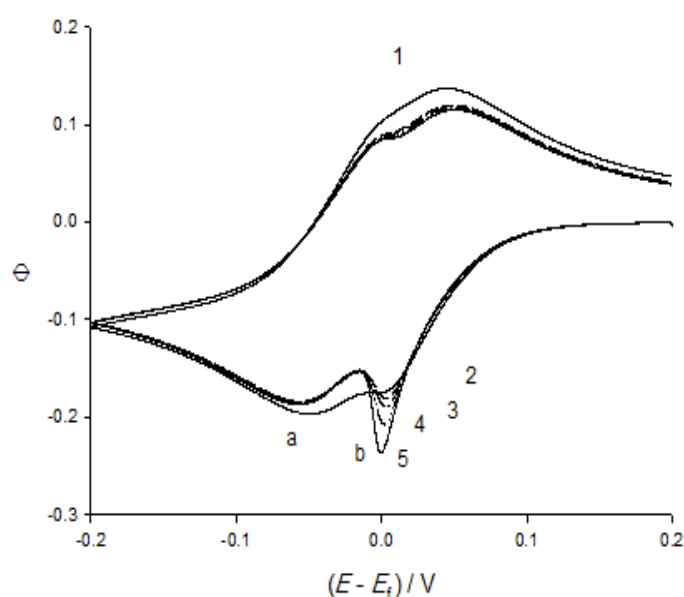


Fig. 6. Dimensionless cyclic voltammograms influenced by the concentration-dependent diffusion coefficient defined by eq. (13): $k=0.4$ (1), 0.35 (2), 0.345 (3), 0.34 (4) and 0.337 (5)

4. CONCLUSIONS

These results can be divided in two groups. If $D(c)$ increases from $c=0$ to c_{\max} (eqs. 7 and 11) the influence of concentration-dependent diffusion coefficient is mostly quantitative and cannot be observed easily. The second group of results is characterized by $D(c)$ that decreases from $c=0$ to c_{\min} (eqs. 9 and 13). Under these conditions the cyclic voltammogram may exhibit two peaks in the cathodic branch. The ratio between minimum currents of these peaks and the potentials of these minima do not depend on the scan rate and this is the indication that the diffusion coefficient depends on the concentration of the product of electrode reaction.

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