

Milivoj Lovrić · Michael Hermes · Fritz Scholz

The effect of the electrolyte concentration in the solution on the voltammetric response of insertion electrodes

Received: 15 December 1997 / Accepted: 5 March 1998

Abstract A solid-state redox reaction involving an insertion of ions is analyzed with respect to the influence of the concentration of inserting ions in the solution phase. The voltammetric response is independent of the mass transfer in the solution provided that $z = (D_{ss}/D_{aq})^{1/2} \rho/[C^+]^*$ is smaller than 0.1 (D_{ss} : diffusion coefficient of the cation C^+ in the crystal; D_{aq} : diffusion coefficient of the cation C^+ in the solution; ρ : density of the solid compound; $[C^+]^*$: concentration of cations in the bulk of the solution). In real cases this condition will be satisfied at solution concentrations above 1 mol/l.

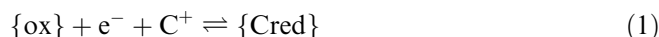
Key words Insertion electrode · Cyclic voltammetry · Electrolyte concentration · Mass transport · Solid-state electrochemistry

Introduction

In a previous paper a model of solid-state redox reaction accompanied by the insertion of cations from the solution was developed for cyclic voltammetry of microcrystals immobilized on the surface of an inert electrode [1]. An excess of dissolved cations was assumed, and the mass transfer in the solution was neglected. In this short communication the influence of diffusion of dissolved cations on cyclic voltammograms of solid microparticles is analyzed theoretically in order to quantitatively verify the above assumption.

Model

It is assumed that a cylinder of the electronically and ionically conductive solid compound is pressed into the surface of a graphite electrode in such a way that only a circular surface of the cylinder is exposed to the solution (see Fig. 1). Being in contact with dissolved ions, this surface acquires the electrode potential at the very beginning of the experiment. In the solid compound, a reversible redox reaction with the insertion of cations C^+ occurs:



The cations can diffuse through the circular surface along the longitudinal axis of the cylinder (Fig. 1). This axis is assumed to be much longer than the diffusion layer in the particle. Under these conditions, the mass transfer can be described by the planar semiinfinite diffusion of cations in two media, namely the solution ($x \leq 0$) and the crystal ($x \geq 0$):

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

where $D = D_{aq}$ and $c = [C^+]$ if $x \leq 0$, and $D = D_{ss}$ and $c = [\text{Cred}]$ if $x \geq 0$. The activities of the oxidized and the reduced forms of the solid compound are proportional to their molar fractions in the mixed crystal which is formed by the redox reaction of Eq. 1. The formal concentrations of these redox components are related to their activities according to the equations $[\text{ox}] = \rho a_{\text{ox}}$ and $[\text{Cred}] = \rho a_{\text{Cred}}$, where ρ is the density of the compound in mol/cm³. In the crystal, the formal concentration of diffusing cations C^+ is equal to the concentration of the reduced component $\{\text{Cred}\}$. So, the starting and boundary conditions for the differential equation labeled Eq. 2 are:

$$\begin{aligned} t = 0, x \leq 0: & \quad [C^+] = [C^+]^* \\ & \quad x \geq 0: \quad [\text{Cred}] = 0, [\text{ox}] = \rho \\ t > 0, x \rightarrow -\infty: & \quad [C^+] \rightarrow [C^+]^* \end{aligned}$$

M. Lovrić (✉)
Center for Marine Research, "Rudjer Bosković" Institute,
P.O. Box 1016, 10001 Zagreb, Croatia

M. Hermes · F. Scholz
Institut für Chemie, Humboldt-Universität zu Berlin,
Hessische Strasse 1-2, D-10115 Berlin, Germany

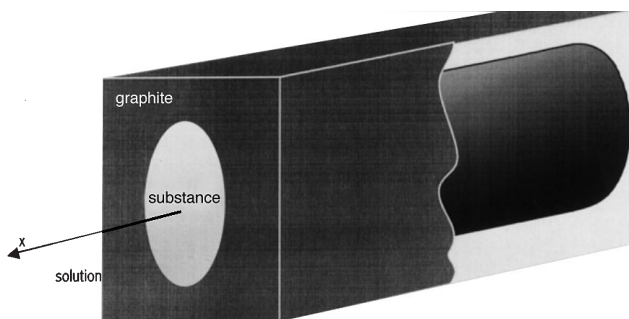


Fig. 1 Solid compound cylinder pressed into a graphite matrix; one circular surface contacts the electrolyte phase

$$\begin{aligned}
 x \geq 0: & \quad [\text{Cred}] + [\text{ox}] = \rho \\
 x \rightarrow \infty: & \quad [\text{Cred}] \rightarrow 0, [\text{ox}] \rightarrow \rho \\
 x = 0: & \quad D_{\text{aq}}(\partial[\text{C}^+]/\partial x) = -i/FS \\
 & \quad D_{\text{ss}}([\partial\text{Cred}]/\partial x) = -i/FS \\
 & \quad [\text{ox}] = [\text{red}^-] \exp[F(E - E_{\text{ox/red}}^0)/RT] \\
 & \quad K = [\text{Cred}][\text{red}^-]^{-1}[\text{C}^+]^{-1}
 \end{aligned}$$

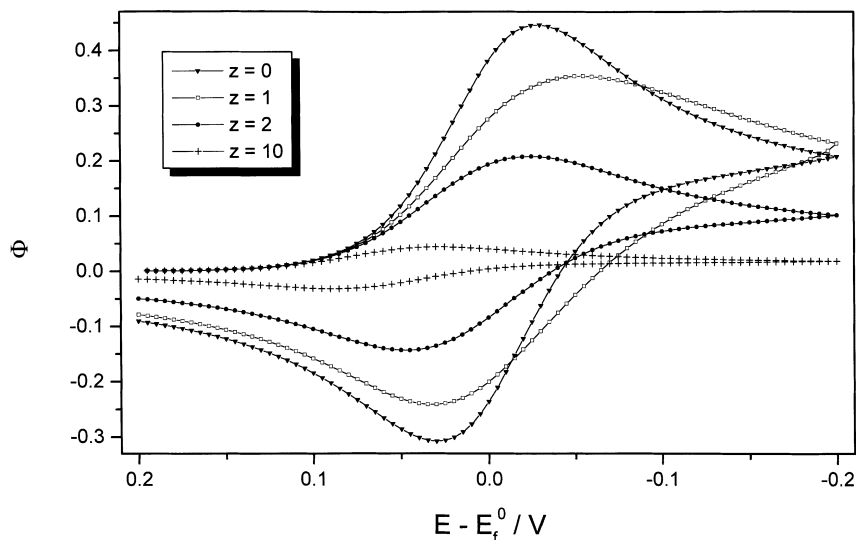
where $[\text{C}^+]$ * is the concentration of cations in the bulk of the solution, S is the area of the solid surface facing the solution, i is the current, $E_{\text{ox/red}}^0$ is the standard potential of the redox reaction $\{\text{ox}\} + e^- \rightleftharpoons \{\text{red}^-\}$, and K is the equilibrium constant of the ion-transfer reaction $\{\text{red}^-\} + \text{C}^+ \rightleftharpoons \{\text{Cred}\}$. The solution of Eq. 2 is a well-known integral equation (Eq. 3), which was solved for cyclic voltammetry by the numerical integration method of Nicholson and Olmstead [3]:

$$z\lambda^2 I^2 - (1 + z + \varepsilon)\lambda I + 1 = 0 \quad (3)$$

where

$$I = \int_0^t \Phi[\pi(t - \tau)]^{-1/2} d\tau,$$

Fig. 2 Theoretical cyclic voltammograms of solid microparticles: $dE = 0.2$ mV and $z = 0, 1, 2,$ and 10



$\Phi = i(FS\rho\lambda)^{-1} D_{\text{ss}}^{-1/2}$ (Φ is the dimensionless current),

$$\lambda = (Fv/RT)^{1/2},$$

$$v = dE/dt,$$

$$\varepsilon = \exp[F(E - E_f^0)RT],$$

$$E_f^0 = E_{\text{ox/red}}^0 + (RT/F)\ln K + (RT/F)\ln[\text{C}^+]*, \text{ and}$$

$$z = (D_{\text{ss}}/D_{\text{aq}})^{1/2} \rho / [\text{C}^+]* \quad (z \text{ is the mass transfer parameter}).$$

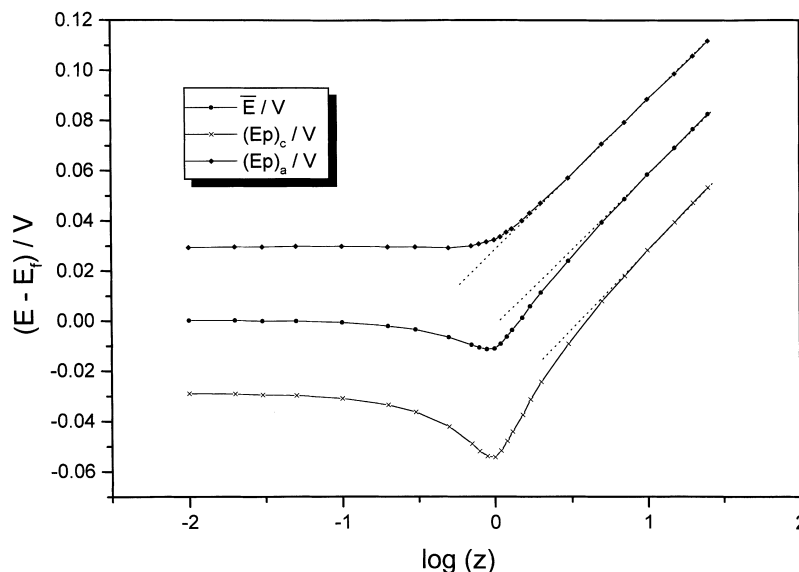
Results and discussion

Cyclic voltammograms of solid microparticles depend on the mass transfer parameter $z = (D_{\text{ss}}/D_{\text{aq}})^{1/2} \rho / [\text{C}^+]*$, where D_{ss} and D_{aq} are diffusion coefficients of the cation C^+ in the crystal and in the solution, respectively, ρ is the density of the solid compound and $[\text{C}^+]$ * is the concentration of cations in the bulk of the solution, both expressed in mol/cm^3 . Some examples are shown in Fig. 2. The dependence of cathodic and anodic peak potentials $(E_p)_c$ and $(E_p)_a$, respectively, and of their median $\bar{E} = (E_{p,c} + E_{p,a})/2$ on the logarithm of the parameter z is shown in Fig. 3. The dependence of dimensionless peak currents $(\Phi_p)_c$ and $(\Phi_p)_a$, respectively, on the logarithm of z is shown in Fig. 4. The voltammograms are independent of the mass transfer in the solution if $z < 0.1$. The peak separation $\Delta E_p = E_{p,a} - E_{p,c}$ is 59 mV, and the median of peaks is equal to the formal potential

$$\bar{E} = E_{\text{ox/red}}^0 + (RT/F)\ln K + (RT/F)\ln [\text{C}^+]*.$$

If $z > 10$, the median depends linearly on the logarithm of z , with a slope of 59 mV and an intercept equal to zero: $E - E_f^0 = 2.3(RT/F) \log z$. This means that the median is independent of the concentration of cations in the solution:

Fig. 3 Dependence of the anodic and cathodic peak potentials $(E_p)_a$ and $(E_p)_c$, respectively and their median \bar{E} on the logarithm of the mass transfer parameter z



$$\bar{E} = E_{\text{ox/red}}^0 + (RT/F)\ln K + (RT/2F)\ln (D_{\text{ss}}/D_{\text{aq}}) + (RT/F)\ln \rho.$$

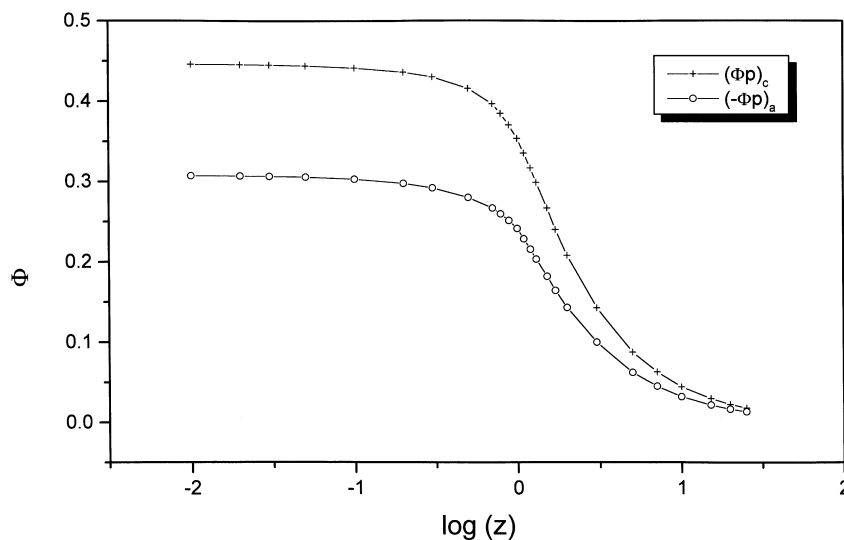
However, under this condition the voltammograms vanish. The most drastic change of the response occurs in the range $0.5 < z < 10$, in which the peak currents decrease from 90% to 10% of the limiting values and the peak separation increases from 70 mV to maximum 87 mV, at $z = 1$, and decreases back to 60 mV for $z > 10$. If $z = 1$, the median potential is 11 mV negative to the formal potential. So, the peak potentials are defined as:

$$(E_p)_{a,c} = E_f^0 - 0.011 \pm 0.043V.$$

Here, to give an example for discussed insertion systems, the concentration of dissolved cations which satisfies the

condition $z < 0.1$ is estimated for Prussian blue, $\text{KFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$. Taking a density for this solid compound of 1.78 g/cm^3 [4] and a molar mass of 397.02 g/mol [5], this gives $\rho = 4.48 \cdot 10^{-3} \text{ mol/cm}^3$. If the ratio $D_{\text{ss}}/D_{\text{aq}}$ is 10^{-3} [6], the concentration of cations must be $[\text{C}^+]^* > 1.42 \cdot 10^{-3} \text{ mol/cm}^3$, or $[\text{C}^+]^* > 1.42 \text{ mol/l}$ to satisfy the condition $z < 0.1$. In case of copper hexacyanoferrate, $\text{K}_2\text{CuFe}(\text{CN})_6$, with a density of $6.64 \cdot 10^{-3} \text{ mol/cm}^3$ [6], the necessary concentration of cations is $[\text{C}^+]^* > 2.1 \cdot 10^{-3} \text{ mol/cm}^3$ or $[\text{C}^+]^* > 2.1 \text{ mol/l}$. Although these values for a particular compound may be significantly different, it is estimated that generally the mass transfer in the solution can be neglected if the concentration of dissolved cations is 1 mol/l or higher. With the help of Fig. 4 it will be possible to determine diffusion coefficients in solids when the diffusion coefficient in solution is known.

Fig. 4 Dependence of absolute values of dimensionless cathodic and anodic peak currents $(\Phi p)_c$ and $(\Phi p)_a$, respectively on the logarithm of the mass transfer parameter z



Acknowledgements The support by the respective Ministries in the framework of a bilateral German-Croatian Scientific Research Program and by Fonds der Chemischen Industrie is gratefully acknowledged.

References

1. Lovrić M, Scholz F (1997) *J Solid State Electrochem* 1:108
2. Jost W (1960) *Diffusion in solids, liquids and gases*. Academic Press, New York, p 68
3. Nicholson RS, Olmstead ML (1972) In: Mattson JS, Mark HB, McDonald HC (eds) *Electrochemistry: calculations simulation and instrumentation*, vol 2. Dekker, New York, p 119
4. Buser HJ, Schwarzenbach D, Peter W, Ludi A (1977) *Inorg Chem* 16:2704
5. Hermes M, Scholz F (1997) *J Solid State Electrochem* 1:215
6. Kahlert H, Retter U, Lohse H, Siegler K, Scholz F (1998) *J Phys Chem B* 102: (in press)