

# Relationship between current response and time in ion transport problem including diffusion and convection.

## 1. An analytical approach

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The mathematical models of the ion transport problem in a potential field are analyzed. Ion transport is regarded as the superposition of diffusion and convection. In the case of pure diffusion model the classical Cottrell's result is studied for a constant as well as for the time dependent Dirichlet data at the electrode. Comparative analysis of the current response  $\mathcal{I}_D = \mathcal{I}_D(t)$  and the classical Cottrellian  $\mathcal{I}_G = \mathcal{I}_G(t)$  is given on the obtained explicit formulas. The approach is extended to find out the current response  $\mathcal{I}_c = \mathcal{I}_c(t)$  corresponding to the diffusion-convection model. The relationship between the current response  $\mathcal{I}_c = \mathcal{I}_c(t)$  and Cottrellian  $\mathcal{I}_G = \mathcal{I}_G(t)$  is obtained in explicit form. This relationship permits one to compare pure diffusion and diffusion-convection models, including asymptotic behaviour of current response and an influence of the convection coefficient. The theoretical result are illustrated by numerical examples.

**KEY WORDS:** ion transport, parabolic problem, current response, Cottrellian

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### 1. Introduction

Mathematical modeling of kinetics and mass-transfer in electrochemical events, even in their simplest statement, generally consists of dealing with various physico-chemical parameters, as well as complicated mathematical problems. In this study we analyse the mathematical model of mass and charge transport in a controlled potential experiment in electrochemistry, called chronoamperometry [1–14]. In the case of two-species (oxidized and reduced species) migrating

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under the influence of the electric field, the mathematical model and governing equations are derived in [1]. This model assumes that the charge flux arises from only diffusion and migration of ions under the influence of the electric field, neglecting the convection, although the ion transport needs to be regarded as a superposition of these three parameters. But even in this, simple from the physico-chemical point of view, model the obtained nonlinear parabolic problem with unknown coefficient and nonlocal additional condition is new in mathematical literature and enough complicated [1,15,16]:

$$\begin{cases} u_t = (g(u)u_x)_x + q'(t)h(u)_x, & (x, t) \in R_+ \times R_+, \quad R_+ := (0, +\infty), \\ u(x, 0) = 0, & x \in R_+, \\ u(0, t) = 1, & t \in R_+, \\ q(t) = \int_0^\infty u(x, t) dx. \end{cases}$$

To the best of our knowledge, this problem, interesting also from the point of view nonlocal inverse/optimal control problems, is not still solved neither mathematically, nor numerically. The only similarity solution of this problem is studied in [15,16], where a variational approach with the conservative finite difference scheme was presented.

The present work is a part of wider research on the analysis of the relationship between current response and time, in ion transport problem including diffusion and convection. The presentations of several aspects of the mass and charge transport of the reduced species in a controlled potential experiment are arranged in the analytical and numerical parts. In this part mathematical model including the convection factor is studied.

In the next section the classical mathematical model, including only diffusion parameter, of chronoamperometry for electroactive species migrating under the influence of the electric field is derived. The relationship between current response and time for the model including diffusion and convection is derived in section 3. In the final section 4 the comparative stability analysis of the considered models is demonstrated.

## 2. Gottrell's model and Cohn's relationship

To derive Gottrell's model of mass and charge transport in a controlled potential experiment, i.e. in chronoamperometry, we denote by  $u = u(x, t)$ ,  $D > 0$  and  $c > 0$ , the concentration, diffusion and convection of the *reduced species*. In the considered model is assumed that there is an electrode at  $x = 0$ , and a medium containing mobile ions and electroactive species in the one-dimensional motion from the electrode to  $x = \infty$ . A potential  $E$  introduced at the initial time  $t = 0$  causes a *reduced fraction* of the *oxidized species* at the surface of the electrode. As oxidized species are reduced at the surface of the electrode, its concentration decreases, and the concentration  $u = u(x, t)$  of the reduced species at

the electrode increases. As a result there arises two diffusion processes: oxidized species diffuse in toward  $x = 0$ , and the reduced species, out into the medium. Therefore ion transport here can be regarded as a superposition of *diffusion*, which is the random motion of small particles immerse in the medium, *migration*, which is a motion under the influence of an electric field, and *convection*, which is a hydrodynamic flow. Exchange of electrons between the surface of the electrode and electroactive species in the time  $t > 0$  gives rise to the *current response*  $\mathcal{I} = \mathcal{I}(t)$ , which is related to the concentration of reduced species by the equation

$$\int_0^\infty u(x, t)dx = \frac{1}{n\mathcal{F}S_e} \int_0^t \mathcal{I}(\tau)d\tau. \tag{1}$$

Here  $n$  is the number of electrons gained by an ion upon reduction,  $F$  is Faraday’s constant and  $S_e$  is the surface of the electrode. The total charge carried by the reduced species is

$$Q(t) = \int_0^t \mathcal{I}(\tau)d\tau. \tag{2}$$

These two definitions permit one to define the total charge  $Q(t)$  via the concentration  $u = u(x, t)$  of the reduced species:

$$Q(t) = n\mathcal{F}S_e \int_0^\infty u(x, t)dx. \tag{3}$$

As was established experimentally [6], for extremely high voltage perturbation, the concentration of oxidized species at the electrode drops immediately to zero, and, at the same time  $t = 0$ , the concentration  $u = u(x, t)$  of the reduced species at the electrode ( $x = 0$ ) is made to jump from zero to  $u_0/z_r$ . Here  $z_r$  and  $z_0$  is the valences of the reduced and oxidized species, which assumed to be integers of the same sign. The process of perturbing the voltage in this manner and studying the resulting current response  $\mathcal{I}_G = \mathcal{I}_G(t)$  as a function of time is known as *chronoamperometry* [2]. In the case of *purely diffusive* flux of electroactive species, the first relationship between the time  $t > 0$  and the current response  $\mathcal{I}_G$  has been experimentally obtained in 1902 by Gottrell. He was found that the current reponse is proportional to  $1/\sqrt{t}$ :

$$\mathcal{I}_G \sim 1/\sqrt{t}.$$

This relationship is defined as *Gottrellian*. The theoretical approval of this result based on the purely diffusive mathematical model

$$\begin{cases} u_t = Du_{xx}, & (x, t) \in R_+ \times R_+, & R_+ = (0, +\infty), \\ u(x, 0) = 0, & x \in R_+, \\ u(0, t) = u_0/z_r, & t \in R_+ \end{cases} \tag{4}$$

was obtained by Cohn in [1]. The analytical formula obtained here for Gottrellian is as follows:

$$\mathcal{I}_G(t) = \frac{n\mathcal{F}S_e u_0}{z_r} \sqrt{\frac{D}{\pi t}}. \quad (5)$$

In order to save the completeness of our study we will derive the same formula (5), but by slightly different way.

The solution  $u = u(x, t)$  of the initial boundary value problem (4) can be obtained from the solution

$$v(x, t) = c_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (6)$$

of the basic parabolic problem

$$\begin{cases} v_t = Dv_{xx}, & (x, t) \in R_+ \times R_+, \\ v(x, 0) = c_0, & x \in R_+, \\ v(0, t) = 0, & t \in R_+, \end{cases}$$

introducing here the new function [17]:

$$u(x, t) = c_0 - v(x, t). \quad (7)$$

The function  $u = u(x, t)$  also satisfies the parabolic equation (5) and the following conditions:

$$\begin{aligned} u(x, 0) &= c_0 - v(x, 0) = 0, \\ u(0, t) &= c_0 - v(0, t) = c_0. \end{aligned}$$

Substituting here  $c_0 = u_0/z_r$  we obtain that the function  $u = u(x, t)$ , given by (7), is the solution of problem (4). Due to (6) and (7) this solution is as follows:

$$u(x, t) = \frac{u_0}{z_r} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right). \quad (8)$$

Here

$$\operatorname{erf}(z) = \frac{\sqrt{\pi}}{2} \int_0^z \exp(-y^2) dy, \quad \operatorname{erfc}(z) = 1 - \operatorname{erf}(z),$$

are error and complementary error functions.

Taking into account definitions (1)–(3) we can calculate Gottrellian as follows:

$$\begin{aligned}
 \mathcal{I}_G(t) := Q'(t) &= \frac{2}{\sqrt{\pi}} \frac{n\mathcal{F}S_e u_0}{z_r} \int_0^\infty \frac{\partial}{\partial t} \left\{ \int_{\frac{x}{2\sqrt{Dt}}}^\infty \exp(-z^2) dz \right\} dx \\
 &= \frac{2}{\sqrt{\pi}} \frac{n\mathcal{F}S_e u_0}{z_r} \int_0^\infty \left\{ \frac{x}{4\sqrt{Dt}} \exp\left(-\frac{x}{2\sqrt{Dt}}\right) \right\} dx \\
 &= \frac{1}{\sqrt{\pi}} \frac{n\mathcal{F}S_e u_0 \sqrt{D}}{z_r t} \int_0^\infty \exp\left(-\left(\frac{x}{2\sqrt{Dt}}\right)\right) d\left(-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right) \\
 &= \frac{n\mathcal{F}S_e u_0}{z_r} \sqrt{\frac{D}{\pi t}},
 \end{aligned}$$

which is Cohn’s result [1].

### 3. The model including diffusion and convection

We consider the same physico-chemical model (1) adding the convection term  $cu_x$ ,  $c > 0$ :

$$\begin{cases} u_t = Du_{xx} - cu_x, & (x, t) \in R_+ \times R_+, \\ u(x, 0) = 0, & x \in R_+, \\ u(0, t) = u_0/z_r, & t \in R_+ \end{cases} \tag{9}$$

In this section we are going to find out an influence of the convective term  $-cu_x$  to the relationship  $\mathcal{I} = \mathcal{I}(t)$ .

Introducing the new function

$$w(x, t) = \exp\left(-\frac{v}{\sqrt{D}}x + v^2t\right) u(x, t), \quad v = \frac{c}{2\sqrt{D}}, \tag{10}$$

we can show that the function  $w = w(x, t)$  satisfies the initial boundary value problem

$$\begin{cases} w_t = Dw_{xx}, & (x, t) \in R_+ \times R_+, \\ w(x, 0) = 0, & x \in R_+, \\ w(0, t) = \mu(t), & t \in R_+, \end{cases} \tag{11}$$

with the time dependent Dirichlet data

$$\mu(t) = \frac{u_0}{z_r} \exp(v^2t), \tag{12}$$

when the function  $u = u(x, t)$  is the solution of problem (9).

The auxiliary problem (11) with the given boundary concentration  $\mu(t)$  at  $x = 0$  can be handled separately. This model corresponds to the exponentially

given concentration of reduced species at  $x = 0$ . The solution of this problem is the integral [17]

$$w(x, t) = \int_0^t \frac{\partial}{\partial t} \operatorname{erfc} \left( \frac{x}{2\sqrt{D(t-\tau)}} \right) \mu(\tau) d\tau.$$

Substituting here (12) we can find the function  $w(x, t)$ :

$$w(x, t) = \frac{u_0 x}{2z_r \sqrt{\pi D}} \int_0^t \frac{1}{(t-\tau)^{3/2}} \exp \left( -\frac{x^2}{4D(t-\tau)} \right) \exp(v^2 \tau) d\tau. \quad (13)$$

By definition (3) we can find the corresponding total charge:

$$\begin{aligned} Q(t) &= \frac{n\mathcal{F}S_e u_0}{2z_r \sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t-\tau}} \exp(v^2 \tau) \left\{ \int_0^\infty \frac{x}{t-\tau} \exp \left( -\frac{x^2}{4D(t-\tau)} \right) dx \right\} d\tau \\ &= \frac{n\mathcal{F}S_e u_0 \sqrt{D}}{z_r \sqrt{\pi}} \int_0^t \frac{1}{\sqrt{t-\tau}} \exp(v^2 \tau) d\tau. \end{aligned}$$

Since

$$\int_0^t \frac{1}{\sqrt{t-\tau}} \exp(v^2 \tau) d\tau = \frac{\sqrt{\pi}}{v} \exp(v^2 t) \operatorname{erf}(v\sqrt{t}),$$

we get

$$Q(t) = \frac{n\mathcal{F}S_e u_0 \sqrt{D}}{z_r v} \exp(v^2 t) \operatorname{erf}(v\sqrt{t}), \quad v = \frac{c}{2\sqrt{D}}.$$

Calculating the first derivative of the function  $Q(t)$  we obtain the current response in the following form:

$$\mathcal{I}_D(t) = \frac{n\mathcal{F}S_e u_0}{z_r} \sqrt{\frac{D}{\pi t}} + \frac{n\mathcal{F}S_e u_0 c}{2z_r} \exp(v^2 t) \operatorname{erf}(v\sqrt{t}). \quad (14)$$

The obtained function  $\mathcal{I}_D = \mathcal{I}_D(t)$  expresses the dependence of the current response on time, when the concentration of the reduced species at the electrode ( $x = 0$ ) is made jump from zero to  $u_0 \exp(v^2 t)/z_r$  exponentially, during the experiment. The first term of the right hand side is exactly the same with Cottrellian, given by (5), i.e.  $\mathcal{I}_c(t) = \mathcal{I}_G(t)$  for  $c = 0$ . The second right hand side term in (14) shows an influence of the concentration  $\mu(t)$  at the electrode, since

$$\frac{n\mathcal{F}S_e u_0 c}{2z_r} \exp(v^2 t) \operatorname{erf}(v\sqrt{t}) = \frac{1}{2} n\mathcal{F}S_e c \mu(t) \operatorname{erf}(v\sqrt{t}),$$

as well as convective factor  $c > 0$  at the initial point  $x = 0$ .

Let use now the above auxiliary problem (11) to derive the current response  $\mathcal{I}_c = \mathcal{I}_c(t)$  in the presence of the convective factor. For this first aim we use formulas (10) and (13) to derive the solution  $u = u(x, t)$  of the parabolic problem (9) in the explicit form. We have

$$u(x, t) = \frac{u_0 x}{2z_r \sqrt{\pi D}} \exp\left(\frac{v}{\sqrt{D}}x - v^2 t\right) \int_0^t (t - \tau)^{-3/2} \exp\left(-\frac{x^2}{4D(t - \tau)}\right) \exp(v^2 \tau) d\tau.$$

Using definition (3) for the total charge we get

$$Q_c(t) = \frac{n\mathcal{F}S_e u_0}{2z_r \sqrt{\pi D}} \int_0^t \frac{-v^2(t - \tau)}{(t - \tau)^{-3/2}} \left\{ \int_0^\infty x \exp\left(-\frac{x^2}{4D(t - \tau)} + \frac{v}{\sqrt{D}}x\right) dx \right\} d\tau.$$

Calculating the integral

$$\int_0^\infty x \exp\left(-\frac{x^2}{4D(t - \tau)} + \frac{v}{\sqrt{D}}x\right) dx = 2D(t - \tau) + c\sqrt{\pi D}(t - \tau)^{3/2}[1 + \operatorname{erf}(v\sqrt{t - \tau})],$$

we have

$$Q_c(t) = \frac{n\mathcal{F}S_e u_0 \sqrt{D}}{z_r \sqrt{\pi}} \int_0^t (t - \tau)^{-1/2} \exp(-2v^2(t - \tau)) d\tau + \frac{n\mathcal{F}S_e u_0 c}{2z_r} \left[ t + \int_0^t \operatorname{erf}(v\sqrt{t - \tau}) d\tau \right].$$

By the change of variables  $z = t - \tau$  we transform the left hand side as follows:

$$Q_c(t) = \frac{n\mathcal{F}S_e u_0 \sqrt{D}}{z_r \sqrt{\pi}} \int_0^t z^{-1/2} \exp(-2v^2 z) dz + \frac{n\mathcal{F}S_e u_0 c}{2z_r} \left[ t + \int_0^t \operatorname{erf}(v\sqrt{z}) dz \right].$$

After the differentiating the right hand side, by the definition  $\mathcal{I}_c(t) := Q'(t)$ , we obtain the current response corresponding to the model with convective term:

$$\mathcal{I}_c(t) = \frac{n\mathcal{F}S_e u_0}{z_r} \sqrt{\frac{D}{\pi t}} \exp(-2v^2 t) + \frac{n\mathcal{F}S_e u_0}{2z_r} c [1 + \operatorname{erf}(v\sqrt{t})], \quad t > 0. \quad (15)$$

Let us compare the current response  $\mathcal{I}_c(t)$ , obtained in the presence of convection, with Gottrellian, given by (5). Evidently for  $c = 0$ ,  $\mathcal{I}_c(t) = \mathcal{I}_G(t)$ . Further, introducing the parameter  $\lambda := (n\mathcal{F}S_e u_0)/z_r$ , which characterizes the physico-chemical constants  $n$ ,  $\mathcal{F}$ ,  $S_e$ , and the concentration  $u_0/z_r$  of the reduced species on the electrode at  $t = 0$ . Then rewriting (15) in the form

$$\mathcal{I}_c(t) = \exp(-2v^2 t) \mathcal{I}_G(t) + \lambda \frac{c}{2} [1 + \operatorname{erf}(v\sqrt{t})], \quad v = \frac{c}{2\sqrt{D}}, \quad t > 0, \quad (16)$$

we obtain the relationship between the current response  $\mathcal{I}_c(t)$  and the classical Cottrellian  $\mathcal{I}_G(t)$ , also an influence of the convection coefficient  $c > 0$ . Thus relationship (16) shows deviation from the classical Cottrellian, and provide information about complex chemical kinetics, in particular, kinetics of heterogeneous ion transfer.

#### 4. Numerical experiments and interpretations

The numerical experiments below are of two groups. In the first series of numerical experiments pure diffusion model is considered. The classical Cottrellian is compared with the current response  $\mathcal{I}_D(t)$ , corresponding to the pure diffusion model with time dependent boundary concentration  $\mu(t)$ , at  $x = 0$ . As was noted above, in classical chronoamperometry the concentration of the reduced species at the point  $x = 0$  made jump from zero to  $u_0/z_r$ . In this case the current response is Cottrellian. The case, when the concentration of the reduced species at the point  $x = 0$  increases exponentially by increasing the time, can be described by the pure diffusive model (11). In this case, as shows formula (14), the current response and relationship  $\mathcal{I}_D \sim t$  includes additional term

$$\frac{n\mathcal{F}S_e u_0 c}{2z_r} \exp(v^2 t) \operatorname{erf}(v\sqrt{t}) = n\mathcal{F}S_e v \sqrt{D} \mu(t) \operatorname{erf}(v\sqrt{t}).$$

Assuming in (12) the parameter  $v$  independent, in particular on the coefficient  $c > 0$ , we can conclude that in the case of the time dependent boundary concentration at  $x = 0$ , the dependence  $\mathcal{I} \sim t$  is not Cottrellian, and has the character

$$\mathcal{I} \sim \frac{1}{\sqrt{t}} + \mu(t).$$

Figure 1 shows the deviations  $\mathcal{I}_D(t) - \mathcal{I}_G(t)$  in the current responses corresponding to constant and exponentially time dependent boundary data at  $x = 0$ . By increasing the time this deviation increases. This figure also shows the asymptotic behaviour of the current response  $\mathcal{I}_D(t)$ , depending on the diffusion coefficient  $D$  and the parameter  $v$ . Therefore the boundary data  $\mu(t)$  has also an important rule in the relationship  $\mathcal{I}_D \sim t$ .

Let us consider now the pure diffusion and diffusion-convection model (9). The main distinguished feature in the behaviour of the current response  $\mathcal{I}_c(t)$  here is that it doesn't tends to zero as time increases. Indeed, since  $\operatorname{erf}(z) \approx 1$  for  $z > 3$ , there exists a time  $t = T$ , for large time

$$\mathcal{I}_c(t) = \exp(-2v^2 t) \mathcal{I}_G(t) + \lambda c, \quad \lambda := \frac{n\mathcal{F}S_e u_0}{z_r}, \quad t > T. \quad (17)$$



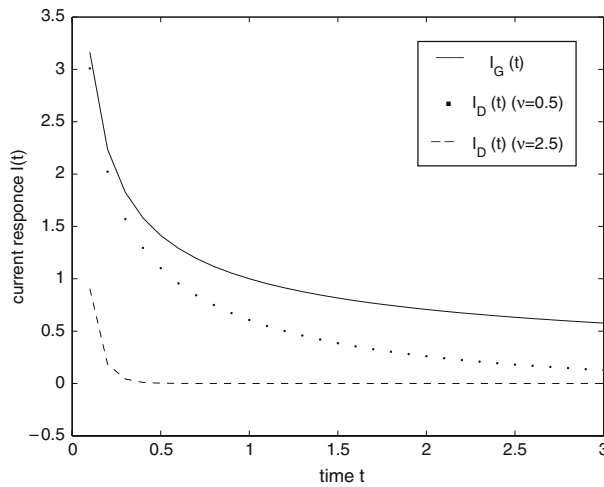


Figure 1. Comparison current responses and Gottrellian for different Dirichlet data:  $D=1$ ,  $\lambda/\sqrt{\pi} = 1$ .

Hence the function  $\mathcal{I}_c(t)$  exponentially decays and tends to the value  $\lambda c$  as  $t \rightarrow \infty$ :

$$\lim_{t \rightarrow \infty} \mathcal{I}_c(t) = \lambda c.$$

Figure 2 shows comparative analysis between the classical Gottrellian  $\mathcal{I}_G(t)$  and the current responses  $\mathcal{I}_c(t)$  for diffusion-convection model. For small values of the convection coefficient  $c > 0$  the deviation  $\mathcal{I}_c(t) - \mathcal{I}_G(t)$  in the current responses is small enough. Thus for  $c = 0.1$  in the time interval  $(0, 10)$  the absolute sup-norm error is

$$\|\mathcal{I}_c - \mathcal{I}_G\|_{L_\infty[0,10]} = 0.088.$$

However this error essentially increases by increasing the convection coefficient  $c > 0$ , as shows figure 2.

### 5. Conclusions

An analytical approach has been developed for the parabolic initial value problem arising in ion transport problem in a controlled potential experiment. The main theme of the study is to study behaviour of the current response depending on time, and a relationship between current responses corresponding to pure diffusion and diffusion-convection models. It is found out that even in the case of pure diffusion model, the current response differs from the classical Gottrellian, if the concentration of the reduced species on the electrode at

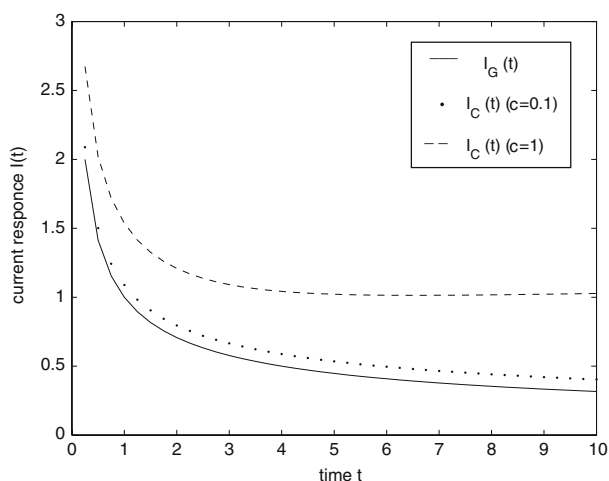


Figure 2. Current responses corresponding to pure diffusion and diffusion-convection models:  $D = 1$ ,  $\lambda/\sqrt{\pi} = 1$ .

the initial time is not constant. Extending the given approach for the diffusion-convection model the explicit analytical formula for the current response  $\mathcal{I}_c$  is obtained. Then the relationship between the current response  $\mathcal{I}_c$  and the classical Cottrellian  $\mathcal{I}_G$  is derived. This relationship shows the degree of influence of the convection factor to the current response  $\mathcal{I}_c$ , permits to estimate the asymptotic behaviour of the current response.

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