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Identification of unknown diffusion coefficient in pure diffusive linear model of chronoamperometry. I. The theory

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Abstract Coefficient identification problem for diffusion equation $u_t(x,t) = (D(x)u_x(x,t))_x$ arising in chronoamperometry is studied. The adjoint problem approach is developed for the case when the output measured data is given in the form of left/right flux. Analytical formulas for determination of the values $D(0)$, $D(L)$ at the endpoints $x = 0; L$, of the unknown coefficient $D(x)$, via the solution $v(x,t)$ of the constant coefficient equation $v_t(x,t) = Dv_{xx}(x,t)$ is obtained. The integral identity relating solutions of the forward and corresponding adjoint problems is derived. This integral identity permits one to prove the monotonicity and invertibility of input-output map, as well as formulate the gradient of the cost functional via the solutions of the direct and adjoint problems.

Keywords Diffusion equation · Chronoamperometry · Adjoint problem approach · Ion transport · Unknown diffusion coefficient · Integral identity · Monotonicity of input-output map

1 Introduction

This article presents a mathematical analysis of the adjoint problem approach for coefficient inverse problem arising in chronoamperometry. Mathematical modeling of ion transport problems in electrochemistry is usually based on the constant coefficient linear diffusion equation $u_t(x,t) = Du_{xx}(x,t)$ [1–4]. Although these models are the quite simplest, they can derive some analytical relationships which permit to understand experiments. Moreover, some results obtained by this way, may play key role

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in finding out some distinguished features of ion transport problems, which can not be estimated experimentally. However due to various distances between the closest cations and anions in lattice, the diffusion coefficient usually depends on the space variable $x > 0$ (see, [5]).

In this study we consider the inverse problem of determining the unknown diffusion coefficient $D(x)$ in the following purely diffusive linear model of chronoamperometry:

$$\begin{cases} u_t(x,t) = (D(x)u_x(x,t))_x, \\ \quad (x,t) \in \Omega_{+\infty} := \{(x,t) \in R^2 : \ 0 < x < \infty, \ 0 < t \leq T\}, \\ u(x,0) = 0, \quad x > 0, \\ u(0,t) = u_0, \quad t \in (0,T]. \end{cases}$$

Here $u(x,t) > 0$ is the concentration of the reduced species and $u_0 > 0$ is the initial concentration at the electrode surface. It is assumed that for extremely high voltage perturbation, the concentration of the oxidized species at the electrode drops immediately to zero, and at the same time, the concentration of the reduced species is made to jump from 0 to u_0.

It is known that [6], the solution $v(x,t)$ of the constant coefficient diffusion equation $v_t(x,t) = Dv_{xx}(x,t)$ tends to zero as $x > 0$ increases infinitely: $v(x,t) \to 0$, as $x \to \infty$. Hence assuming $L > 0$ large enough, we may consider the above initial-boundary value problem not in the infinite domain $\Omega_{+\infty}$, but in the finite parabolic domain $\Omega_T := \{(x,t) \in R^2 : \ 0 < x < L, \ 0 < t \leq T\}$, with the Dirichlet condition $u(L,t) = 0$ at $x = L$:

$$\begin{cases} u_t(x,t) = (D(x)u_x(x,t))_x, \\ \quad (x,t) \in \Omega_T := \{(x,t) \in R^2 : \ 0 < x < L, \ 0 < t \leq T\}, \\ u(x,0) = 0, \quad x \in (0,L), \\ u(0,t) = u_0, \quad u(L,t) = 0, \quad t \in (0,T]. \end{cases} \tag{1}$$

Since the diffusion coefficient $D(x)$ is assumed to be unknown and needs to be determined, one needs to impose an additional condition. Most appropriate, from the physical and mathematical points of view, is the left flux at $x = 0$:

$$\varphi_l(t) := -D(0)u_x(0,t), \quad t \in (0,T]. \tag{2}$$

The above problem (1)–(2) is defined to be *the coefficient inverse problem for pure diffusive linear model of chronoamperometry*.

The function $\varphi_l(t)$ represents the measured flux at the electrode surface (left flux) and is defined to be *measured output data*. In this context the parabolic problem (1) will be referred as a *direct (forward) problem*, with the *inputs* u_0 and $D(x)$. For a given coefficient $D(x)$ solution of the direct problem (1), corresponding to this coefficient, will be defined as $u = u(x,t; D(x))$. The function $\varphi_{ls}(t) := (-D(x)u_x(x,t; D(x))_{x=0}$, defined via this solution will be referred as the *synthetic output data* (theoretical value of the left flux). With this definition the additional condition (2) can also be rewritten as follows:

$$(-D(x)u_x(x,t; D(x))_{x=0} = \varphi_l(t), \quad t \in (0,T].$$

Let $u = u(x, t; D(x))$ be the unique solution of the direct problem (1) for a given coefficient $D(x) \in \mathcal{D}$, from some class of admissible coefficients $\mathcal{D}$. Then the inverse problem (1)–(2) can be formulated in the following operator equation form:

$$\Phi(D)(t) = \varphi_l(t), \quad \varphi_l \in \mathcal{F}, \quad t \in (0, T], \tag{3}$$

where $\mathcal{F}$ is the set of admissible fluxes. The mapping

$$\Phi(D)(t) := (-D(x)u_x(x, t; D(x)))_{x=0}, \quad D(x) \in \mathcal{D}, \quad t \in (0, T] \tag{4}$$

is defined to be *the input-output map*: $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$.

Therefore the inverse problem (1)–(2) with the given measured output data $\varphi_l \in \mathcal{F}$ can be reduced to the solution of the nonlinear Eq. (3) or to inverting the coefficient-flux (or input-output) map $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$.

Three classes of well-known methods are widely used for identifying the unknown diffusion coefficient from various types of measured output data: output least squares (OLS) [7–9], equation error method [10–12], and adjoint problem approach [13–15]. Comparative analysis of these methods is given in [14,15]. Different from the previous two classes of methods, the adjoint problem approach permits one to prove not only monotonicity and then invertibility of the input-output mappings of type (4), but also to establish a relationship between the solution of the direct and corresponding adjoint problems in the form of integral identity. These type of integral identities play an important role in construction an effective computational algorithms for numerical reconstruction of the unknown diffusion coefficient in various applications [14,15]. For coefficient inverse problem of chronoamperometry the numerical algorithm of reconstruction the unknown diffusion coefficient $D(x)$ is proposed in the second part of this study.

In this paper an implementation of the adjoint problem approach to the coefficient inverse problem of chronoamperometry is studied. In Sect. 2 analytical formulas for determination of the endpoint values $D(0)$, $D(L)$ of the unknown coefficient via the solution of the constant coefficient equation $v_t(x, t) = Dv_{xx}(x, t)$ is given. The integral identity relating the forward and corresponding adjoint problems is derived Sect. 3. Based on this integral identity 3 Fréchet differentiability of the corresponding cost functional is proved, and a formula the gradient of this functional is obtained via the solutions of the direct and adjoint problems. In the final Sect. 4 monotonicity and invertibility of the input-output mapping is proved.

2 Analytical formulas for the values $D(0)$, $D(L)$ of the unknown coefficient

Consider ion transport problem within the pure diffusive linear model, assuming that the diffusion coefficient is constant:

$$\begin{cases} v_t(x, t) = Dv_{xx}(x, t), & (x, t) \in \Omega_{+\infty}, \\ v(x, 0) = 0, & x > 0, \\ v(0, t) = u_0, & t > 0. \end{cases} \tag{5}$$

We use the analytical solution

$$v(x,t) = u_0\, erfc\left(\frac{x}{2\sqrt{Dt}}\right), \quad x > 0, \ \ t > 0 \tag{6}$$

of this problem to find the left flux $\varphi_0(t)$ at the electrode surface $x = 0$. We have

$$[v_x(x,t)]_{x=0} = u_0 \frac{\partial}{\partial x}\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-y^2)dy\right]_{x=0}, \quad t > 0, \tag{7}$$

and hence

$$v_x(0,t) = -\frac{u_0}{\sqrt{\pi Dt}}, \quad t > 0.$$

According to the definition $\varphi_0(t) := -Dv_x(0,t)$ of the left flux, this implies:

$$\varphi_0(t) = u_0\sqrt{\frac{D}{\pi t}}, \quad t > 0. \tag{8}$$

Hence for pure diffusive linear model of ion transport problem, the analytical formula for the left flux is defined by formula (8). With the formula

$$\mathcal{I}_C(t) = n\mathcal{F}S_e u_0\sqrt{\frac{D}{\pi t}}, \quad t > 0,$$

for the Cottrellian $\mathcal{I}_C(t)$ (see, [6]), this formula implies that the following relationship holds between the left flux $\varphi_0(t)$ and the Cottrellian $\mathcal{I}_C(t)$:

$$\varphi_0(t) = (n\mathcal{F}S_e)^{-1}\mathcal{I}_C(t), \quad t > 0.$$

In view of inverse problems this means that for pure diffusive linear model of ion transport problem *the left flux $\varphi_0(t)$ and the Cottrellian $\mathcal{I}_C(t)$ are equivalent measured output data*.

Our goal is use of the auxiliary problem (5), and additional condition (2) for determination of the value $D(0)$ of the unknown coefficient $D(x)$. For this aim let us consider the initial-boundary value problem (5) in the finite parabolic domain $\Omega_T := \{(x,t) \in R^2 : \ 0 < x < L, \ 0 < t \leq T\}$:

$$\begin{cases} v_t(x,t) = Dv_{xx}(x,t), \quad (x,t) \in \Omega_T, \\ v(x,0) = 0, \quad x \in (0,L), \\ v(0,t) = u_0, \quad v(L,t) = \mu_1(t), \quad t \in (0,T], \end{cases} \tag{9}$$

where

$$\mu_1(t) = u_0\, erfc\left(\frac{L}{2\sqrt{Dt}}\right), \quad t \in (0, T],$$

according to formula (6). As in the case of the forward problem (1), taking $L > 0$ large enough we may assume that $\mu_1(t) = 0$. Formula (6) permits one find also the right flux $\varphi_1(t) := -Dv_x(L, t)$:

$$\varphi_1(t) = u_0\sqrt{\frac{D}{\pi t}}\exp\left(-\frac{L^2}{4Dt}\right), \quad t > 0. \tag{10}$$

The following lemma establishes an analytical formulas for the value $D(0)$ of the unknown coefficient $D(x)$ at the endpoint $x = 0$, via flux data $\varphi_{ls}(t)$, and the corresponding solution of problem (9).

Lemma 1 *Let $D(x) \in L_\infty[0, L]$, and $\varphi_l(t) > 0$ be given noise free measured output data in the inverse problem (1)–(2), i.e. $\varphi_l(t) \equiv \varphi_{ls}(t)$. Then the value $D(0)$ of the unknown diffusion coefficient $D(x)$ can be determined from the solution $v(x, t; D(0))$ of the parabolic problem (9) as follows*

$$D(0) = -\lim_{t\to 0}\frac{\varphi_l(t)}{v_x(0, t; D(0))}, \tag{11}$$

where $v(x, t; D(0))$ is the solution of problem (9), corresponding to the coefficient $D = D(0)$.

Proof Let us define the function $w(x, t) = u(x, t) - v(x, t)$, where $u(x, t) := u(x, t; D(x))$ and $v(x, t) := v(x, t; D(0))$ are the solutions of parabolic problems (1) and (9), respectively. Then

$$w_t = u_t - v_t = (D(0)w_x)_x + ((D(x) - D(0))u_x)_x,$$

and the function $w = w(x, t)$ is the solution of the following initial boundary value problem:

$$\begin{cases} w_t - D(0)w_{xx} = F_w(x, t), & (x, t) \in \Omega_T, \\ w(x, 0) = 0, & x \in (0, L), \\ w(0, t) = w(L, t) = 0, & t \in (0, T], \end{cases} \tag{12}$$

and $F_w(x, t) = ((D(x) - D(0))u_x)_x$. Multiply the both sides of Eq. (12) to an arbitrary function $\psi_x(x, t)$ and integrating on Ω_T we obtain the following integral identity:

$$\int\!\!\int_{\Omega_T}[w_t - D(0)w_{xx}]\psi_x(x, t)dxdt = \int\!\!\int_{\Omega_T}((D(x) - D(0))u_x)_x\psi_x(x, t)dxdt.$$

Integrating by parts yields:

$$\int_0^L (w\psi_x)_{t=0}^{t=T}\, dx - \int\int_{\Omega_T} w\psi_{xt} dxdt - D(0)\int_0^T (w_x\psi_x)_{x=0}^{x=L}\, dt$$
$$+ D(0)\int\int_{\Omega_T} w_x\psi_{xx} dxdt = \int\int_{\Omega_T} ((D(x)-D(0))u_x)_x \psi_x dxdt. \quad (13)$$

Now we require that the function $\psi(x,t)$ is chosen to be the solution of the following backward parabolic problem

$$\begin{cases} \psi_t + D(0)\psi_{xx} = F_\psi(x,t), & (x,t)\in\Omega_T, \\ \psi(x,T) = 0, & x\in(0,L), \\ \psi_x(0,t) = \psi_x(L,t) = 0, & t\in(0,T), \end{cases} \quad (14)$$

with an arbitrary (integrable) function $F_\psi(x,t)$ which will be defined below. Note that problem (14) with the backward parabolic equation $\psi_t + D(0)\psi_{xx} = F_\psi(x,t)$ is well-posed one, due to the condition $\psi(x,T) = 0$ at the final time.

We define the first three integrals on the left hand side of (13) as I_i, $i = 1,2,3$, sequentially, from the left to right, and calculate these integrals. The first and third integrals I_1 and I_3 are zero, due to the homogeneous initial/final conditions $w(x,0) = 0$, $\psi_x(x,T) = 0$, and the boundary conditions $\psi_x(0,t) = \psi_x(L,t) = 0$. Further,

$$I_2 = \int_0^T (w\psi_t)_{x=0}^{x=L} dx - \int\int_{\Omega_T} w_x\psi_t dxdt = -\int\int_{\Omega_T} w_x\psi_t dxdt,$$

due to the conditions $w(0,t) = w(L,t) = 0$.

We transform now the right hand side integral in identity (13), integrating it by parts and using the homogeneous boundary conditions $\psi_x(0,t) = \psi_x(L,t) = 0$. Then we have:

$$\int\int_{\Omega_T} ((D(x)-D(0))u_x)_x \psi_x dxdt = -\int\int_{\Omega_T} (D(x)-D(0))u_x\psi_{xx} dxdt.$$

Substituting these in the integral identity (13) we get:

$$\int\int_{\Omega_T} [\psi_t + D(0)\psi_{xx}] w_x dxdt = -\int\int_{\Omega_T} (D(x)-D(0))u_x\psi_{xx} dxdt.$$

Since the function $\psi(x,t)$ is the solution of the backward parabolic equation $\psi_t + D(0)\psi_{xx} = F_\psi(x,t)$, this yields:

$$-\iint_{\Omega_T} (D(x) - D(0)) u_x \psi_{xx} dxdt = \iint_{\Omega_T} F_\psi(x,t) w_x dxdt. \tag{15}$$

Let us estimate the left hand side integral by using continuity of the function $D(x)$ and arbitrarily of the function $F_\psi(x,t)$. Due to arbitrarily of the function $F_\psi(x,t)$, we require that $F_\psi(x,t) \in L_2(0,T; L_2(0,L))$, and

$$\begin{cases} Supp F_\psi \subset (0,\eta) \times (0,\tau) \subset \Omega_T, \quad \eta, \tau > 0; \\ F_\psi(x,t) \equiv 1, \;\; \forall (x,t) \in Supp F_\psi. \end{cases} \tag{16}$$

By the improved regularity property of solution $\psi(x,t)$ of the backward parabolic problem (14), this implies: $\psi \in L_2(0,T; H^2(0,L)) \cap L_\infty(0,T; H^1(0,L))$ (see, [16], p. 360), and

$$\|\psi\|_{L_2(0,T;H^2(0,L))} \le c_\psi \|F_\psi\|_{L_2(0,T;L_2(0,L))}, \quad c_\psi > 0. \tag{17}$$

Further, by H^1-continuity of the solution $u \in L_\infty(0,T; H^1(0,L))$ of the forward problem (1) with respect to input data, we have

$$ess\ sup_{[0,T]} \|u\|_{H^1(0,L)} + \|u\|_{L_2(0,T;H^2(0,L))} \le c_u u_0, \quad c_u > 0. \tag{18}$$

Now we may estimate the left hand side integral (15) separately, in $(0,\delta) \times (0,T]$ and $(\delta, L) \times (0,T]$:

$$\begin{aligned} &\left| \int_0^L \int_0^T (D(x) - D(0)) u_x \psi_{xx} dxdt \right| \\ &\quad \le \left| \int_0^\delta \int_0^T (D(x) - D(0)) u_x \psi_{xx} dxdt \right| + \left| \int_\delta^L \int_0^T (D(x) - D(0)) u_x \psi_{xx} dxdt \right|. \end{aligned} \tag{19}$$

Due to the continuity of the function $D(x)$, for we have: for all $\varepsilon > 0$ there exists $\delta > 0$ such that $|D(x) - D(0)| < \varepsilon$, for all $x \in (0,\delta)$. Hence

$$\left| \int_0^\delta \int_0^T (D(x) - D(0)) u_x \psi_{xx} dxdt \right| \le c_1 \varepsilon, \tag{20}$$

where

$$c_1 = \|u_x\|_{L_2((0,\delta)\times(0,T))}\|\psi_{xx}\|_{L_2((0,\delta)\times(0,T))} > 0.$$

Using the boundedness of the function $D(x)$, in the second right hand side integral in (19) we have:

$$\left|\int_\delta^L\int_0^T (D(x)-D(0))u_x\psi_{xx}dxdt\right| \le c_D\left|\int_\delta^L\int_0^T u_x\psi_{xx}dxdt\right|,$$

where $c_D = \sup_{[0,L]}|D(x)-D(0)|$. Estimating the above right hand side integral we obtain:

$$\begin{aligned}
&\left|\int_\delta^L\int_0^T (D(x)-D(0))u_x\psi_{xx}dxdt\right| \\
&\quad\le c_D\int_0^T \|u_x\|_{L_2(\delta,L)}\|\psi_{xx}\|_{L_2(\delta,L)}dt \\
&\quad\le c_D\ ess\ sup_{[0,T]}\|u_x\|_{L_2(\delta,L)}\int_0^T \|\psi_{xx}\|_{L_2(\delta,L)}dt \\
&\quad\le c_D\sqrt{T}\ ess\ sup_{[0,T]}\|u_x\|_{L_2(\delta,L)}\left(\int_0^T \|\psi_{xx}\|^2_{L_2(\delta,L)}dt\right)^{1/2} \\
&\quad\le c_D\sqrt{T}\ ess\ sup_{[0,T]}\|u_x\|_{L_2(0,L)}\ \|\psi\|_{L_2(0,T;H^2(0,L))}.
\end{aligned}$$

Taking into account here estimates (17) and (18) we conclude

$$\left|\int_\delta^L\int_0^T (D(x)-D(0))u_x\psi_{xx}dxdt\right| \le c_2\|F_\psi\|_{L_2(0,T;L_2(0,L))},\quad c_2 = c_Dc_\psi c_u u_0 > 0.$$

This, with (20), implies the following estimate for the left hand side integral of (15):

$$\left|\int_0^L\int_0^T (D(x)-D(0))u_x\psi_{xx}dxdt\right| \le c_1\varepsilon + c_2\|F_\psi\|_{L_2(0,T;L_2(0,L))},\quad c_1,\ c_2 > 0.$$

Denoting by $c_0 = 2\max\{c_1;\ c_2\}$, we can estimate the right hand side integral of (15) as the follows:

$$\left| \int\int_{\Omega_T} F_\psi(x,t)\psi_x dx dt \right| \le 2c_0 \left[\varepsilon + \|F_\psi\|_{L_2(0,T;L_2(0,L))} \right], \quad c_0 > 0.$$

Let us require that $\|F_\psi\|_{L_2(0,T;L_2(0,L))} \le \varepsilon$, by choosing the parameters $\eta,\ \tau > 0$ in (16) small enough. Here $\varepsilon > 0$ is the above given arbitrary small parameter. Then taking into account in the above left hand side integral also the property $F_\psi(x,t) = 1$, $\forall(x,t) \in Supp F_\psi$ of the function $F_\psi(x,t)$, finally we obtain:

$$\left| \int_0^\eta \int_0^\tau w_x(x,t) dx dt \right| \le c_0 \varepsilon, \quad \forall \varepsilon > 0.$$

This estimate with (16) implies

$$\lim_{t\to 0} \lim_{x \to 0} w_x(x,t) = 0,$$

or

$$\lim_{t\to 0} [u_x(0,t; D(0)) - v_x(0,t; D(0))] = 0.$$

Hence,

$$\lim_{t\to 0} \frac{u_x(0,t; D(0))}{v_x(0,t; D(0))} = 1.$$

By the definition of the output (flux) data $\varphi_{ls}(t) := -D(0)u_x(0,t; D(0))$, this implies the proof. □

Combining this result with formula (8) we obtain the following result.

Corollary 1 *Let conditions of Lemma 1 hold. Then value $D(0)$ of the unknown diffusion coefficient $D(x)$ can be determined from the solution $v(x,t; D(0))$ of the parabolic problem (9) as follows*

$$D(0) = \frac{\pi}{u_0^2} \left(\lim_{t\to 0} \sqrt{t}\, \varphi_l(t) \right)^2. \tag{21}$$

The similar formula at $x = L$ can be obtained by the same way, introducing the function $v(x,t; D(1))$, which is the solution of the parabolic problem (9).

Lemma 2 *Let $D(x) \in L_\infty[0, L]$, and $\varphi_r(t) > 0$ be given noise free measured output data in the inverse problem (1)–(2), i.e. $\varphi_r(t) \equiv \varphi_{rs}(t)$, and $\varphi_{rs}(t) := -D(L)u(L, t; D(L))$. Then the value $D(L)$ of the unknown diffusion coefficient $D(x)$ can be determined as follows:*

$$D(L) = -\lim_{t\to 0} \frac{\varphi_{rs}(t)}{v_x(L, t; D(L))} \tag{22}$$

where $v(x, t; D(L))$ is the solution of problem (9), corresponding to the coefficient $D = D(L)$.

The proof of this lemma is similar to the above proof scheme. One only needs to take the compact support of the function $F_\psi(x, t)$ as follows: $Supp F_\psi \subset (L-\eta, L)\times(0, \tau) \subset \Omega_T$.

Remark 1 If the length parameter $L > 0$ is not large enough, and $\mu_1(t) \neq 0$ in (9), then one needs to impose the same boundary condition $u(L, t) = \mu_1(t)$ in the forward problem (1) instead of the homogeneous condition $u(L, t) = 0$. In this case the solution $w(x, t)$ of the parabolic problem (12) will again satisfy the homogeneous boundary conditions, and the assertion of the above lemma will remain true.

3 The integral identity relating the forward and adjoint problems. Gradient of the cost functional

The above results show that having the flux data $\varphi_l(t)$ and $\varphi_r(t)$, we can find directly the values $D(0)$, $D(1)$ of the unknown coefficient $D(x)$, via the solution of the parabolic problem (9). This problem will be defined as the *basic problem*. Let us construct now the integral identity relating the forward problem (1) with corresponding adjoint problem, via the output data.

Lemma 3 *Let $u_1(x, t) = u(x, t; D_1(x))$ and $u_2(x, t) = u(x, t; D_2(x))$ be solutions of the direct problem (1) corresponding to the coefficients $D_1(x), D_2(x) \in L_\infty[0, L]$. Suppose that $\varphi_{ls}^{(j)}(t) = -D_j(0)u(0, t; D_j(0))$, $j = 1, 2$, are corresponding outputs, and $\Delta\varphi_{ls}(t) = \varphi_{ls}^{(1)}(t) - \varphi_{ls}^{(2)}(t)$, $\Delta D(x) = D_1(x) - D_2(x)$. If $D_1(0) = D_2(0)$, then for each $\tau \in (0, T]$ the following integral identity holds:*

$$\int\int_{\Omega_\tau} \Delta D(x)u_{2x}(x, t)\psi_x(x, t)dxdt = \int_0^\tau p(t)\Delta\varphi_{ls}(t)dt, \quad \forall\tau \in (0, T], \tag{23}$$

where the function $\psi(x, t) = \psi(x, t; p)$ is the solution of the following backward parabolic problem

$$\begin{cases} \psi_t + (D_1(x)\psi_x)_x = 0, \quad (x, t) \in \Omega_\tau := (0, L) \times (0, \tau], \\ \psi(x, \tau) = 0, \quad x \in (0, L), \\ \psi(0, t) = p(t), \quad \psi(L, t) = 0, \quad t \in (0, \tau), \end{cases} \tag{24}$$

with arbitrary Dirichlet data $p(t) \in C(0, T]$.

Proof The function $w(x,t) = u_1(x,t) - u_2(x,t)$ solves the following initial boundary value problem:

$$\begin{cases} w_t - (D_1(x)w_x)_x = (\Delta D(x)u_{2x})_x, & (x,t) \in \Omega_\tau, \\ w(x,0) = 0; \quad x \in (0,L), \\ w(0,t) = 0, \quad w(L,t) = 0, \quad t \in (0,\tau). \end{cases}$$

Multiply both sides of the above equation by an arbitrary function $\psi(x,t)$ and integrate by parts on Ω_τ. Then we obtain:

$$\int_0^L (w\psi)_{t=0}^{t=\tau} dx - \iint_{\Omega_\tau} w\psi_t dxdt = \int_0^\tau (D_1(x)w_x\psi)_{x=0}^{x=L} dt - \int_0^\tau (D_1(x)w\psi_x)_{x=0}^{x=L} dt$$
$$+ \iint_{\Omega_\tau} w(D_1(x)\psi_x)_x dxdt + \int_0^\tau (\Delta D(x)u_{2x}\psi)_{x=0}^{x=L} dt - \iint_{\Omega_\tau} \Delta D(x)u_{2x}\psi_x dxdt$$

Now we require that the function $\psi(x,t)$ is the solution of the backward parabolic problem (24). Then due to the homogeneous initial and boundary conditions $w(x,0) = w(0,t) = w(L,t) = 0$, and also the conditions $\psi(x,\tau) = \psi(L,t) = 0$, $\psi(0,t) = p(t)$, the above integral identity implies:

$$\iint_{\Omega_\tau} \Delta D(x)u_{2x}(x,t)\psi_x(x,t)dxdt = -\int_0^\tau \Delta D(0)u_{2x}(0,t)p(t)dt$$
$$-\int_0^\tau D_1(0)w_x(0,t)p(t)dt.$$

We transform the right hand side terms under the integral, using the condition $D_1(0) = D_2(0)$ and the relations

$$\begin{aligned} &-\Delta D(0)u_{2x}(0,t) - D_1(0)w_x(0,t) = -[D_1(0) - D_2(0)]u_{2x}(0,t) \\ &-D_1(0)[u_{1x}(0,t) - u_{2x}(0,t)] = D_2(0)u_{2x}(0,t) - D_1(0)u_{1x}(0,t) \\ &\quad = -D_1(0)w_x(0,t) = \Delta\psi_{ls}(t). \end{aligned}$$

Substituting this into the above identity we obtain the required integral identity (19). □

Corollary 1 *Let us assume in Lemma 3 that* $u(x,t) + \Delta u(x,t)$ *and* $u(x,t)$ *instead of* $u_1(x,t)$ *and* $u_2(x,t)$*, respectively (which means* $D_1(x) = D(x) + \Delta D(x)$, $D_2(x) =$

$D(x)$). If $\Delta D(0) = 0$, then for each $\tau \in (0, T]$ the following integral identity holds:

$$\iint_{\Omega_\tau} \Delta D(x) u_x(x,t) \psi_x(x,t) dx dt = \int_0^\tau p(t) \Delta\varphi_{ls}(t) \psi dt, \quad \forall \tau \in (0, T], \tag{25}$$

where $u(x,t) := u(x,t; D(x))$ is the solution of the direct problem (1), $\psi(x,t) = \psi(x,t;p)$ is the solution of the backward parabolic problem

$$\begin{cases} \psi_t + ((D(x) + \Delta D(x))\psi_x)_x = 0, \quad (x,t) \in \Omega_\tau := (0, L) \times (0, \tau], \\ \psi(x, \tau) = 0, \quad x \in (0, L), \\ \psi(0,t) = p(t), \quad \psi(L,t) = 0, \quad t \in (0, \tau), \end{cases} \tag{26}$$

and the function $p(t) \in C(0, T]$ is an arbitrary Dirichlet data.

The backward parabolic problem (26) will be defined as *the adjoint problem, corresponding to the forward problem* (1).

The integral identity (25) can be used as an important tool for numerical solution of the inverse problem (1)–(2). This approach will be discussed in the second part of the study.

Note that the similar integral identity can be derived for the case when the measured output data is given in the form of the right flux.

Let us reformulate now the inverse problem (1)–(2) as a variational problem, by using the quasi-solution approach [17]. Introducing the cost functional:

$$J(D) = \frac{1}{2} \int_0^T [\varphi_{ls}(t) - \varphi_l(t)]^2 dt, \quad D \in \mathcal{D}, \tag{27}$$

we can formulate the inverse problem (1)–(2) as the minimization problem

$$J(D_*) = \inf_{D \in \mathcal{D}} J(D), \tag{28}$$

for the cost functional $J(D)$, defined on the set of admissible coefficients $\mathcal{D}$. Here $\varphi_{ls}(t) := (-D(x)u_x(x,t; D(x)))_{x=0}$ is the output data. Any gradient method related to the minimization problem (28) requires a'priori information about the gradient $J'(D)$ of the cost functional (27). Using the integral identity (25) we can derive the gradient formula for the cost functional $J(D)$. For this aim, let us consider the first variation $\Delta J(D) := J[D + \Delta D] - J(D)$ of the cost functional (27). We have

$$\Delta J(D) = \frac{1}{2} \int_0^T \Big\{ [\varphi_l(t) + ((D + \Delta D) u_x(x,t; D + \Delta D))_{x=0}]^2 \\ - [\varphi_l(t) + (D u_x(x,t;D))_{x=0}]^2 \Big\} dt$$

Using here the notations $\Delta u_x = u_x(x,t;D+\Delta D) - u_x(x,t;D)$, $\Delta\varphi_{ls}(t) := (-(D+\Delta D)u_x(x,t;D+\Delta D))_{x=0} - (-Du_x(x,t;D))_x$, and taking into account that $\Delta\varphi_{ls}(t) = -[D\Delta u_x(x,t;D) + \Delta D u_x(x,t;D) + \Delta D\Delta u(x,t;D)]_{x=0}$, we get

$$\Delta J(D) = \frac{1}{2}\int_0^T [2\varphi_l(t) - 2\varphi_{ls}(t) + \Delta\varphi_{ls}(t)]\,\Delta\varphi_{ls}(t)dt.$$

Thus for the first variation of the cost functional (27) we obtain the following formula

$$\Delta J(D) = \int_0^T [\varphi_l(t) - \varphi_{ls}(t)]\Delta\varphi_{ls}(t)dt + \frac{1}{2}\int_0^T [\Delta\varphi_{ls}(t)]^2 dt. \tag{29}$$

Let us choose now the arbitrary Dirichlet data $p(t) \in C(0,T]$ in (26) as follows: $p(t) = \varphi_l(t) - \varphi_{ls}(t)$. Then for $\tau = T$ the integral identity (25) becomes

$$\int\int_{\Omega_T} \Delta D(x)u_x(x,t)\psi_x(x,t)dxdt = \int_0^T [\varphi_l(t) - \varphi_{ls}(t)]\Delta\varphi_{ls}(t)\psi dt.$$

This identity with (29) imply:

$$\Delta J(D) = \int\int_{\Omega_T} \Delta D(x)u_x(x,t)\psi_x(x,t)dxdt + \frac{1}{2}\int_0^T [\Delta\varphi_{ls}(t)]^2 dt.$$

Let us rewrite this formula taking into account the definition

$$\Delta J(D) = \langle J'(D), \Delta D\rangle + o\left(\|\Delta D\|^{\sigma}_{H^0(0,L)}\right), \quad \sigma \geq 1$$

of the Fréchet differential:

$$\Delta J(D) = \int_0^L \left[\int_0^T u_x(x,t)\psi_x(x,t)dt\right]\Delta D(x)dx + \frac{1}{2}\|\Delta\varphi_{ls}\|^2_{H^0(0,T)}, \tag{30}$$

where H^0 is the Sobolev space.

This formula provides further insight into the gradient of the functional $J(D)$ via the solution of the adjoint problem (26). By the above definition of the Fréchet differential, one needs to show only that the last term on the right hand side of (30) is of order $o\left(\|\Delta D\|^{\sigma}_{H^0(0,L)}\right)$, with $\sigma \geq 1$. This assertion can be obtained from the result given in [18].

Lemma 4 *Let solutions $u(x,t)$ and $\psi(x,t)$ of the direct and adjoint problems belong to the class $L_2(0,T;H^2(0,L)) \cap L_\infty(0,T;H^1(0,L))$. Then the cost functional (27) is Fréchet-differentiable, $J(D) \in C^1(\mathcal{D})$, and its Fréchet derivative at $D \in \mathcal{D}$ can be defined by the solutions of the direct problem (1) and adjoint problem (26) as follows:*

$$J'(D) = (u_x, \psi_x)_{H^0(0,T)}. \tag{31}$$

4 Monotonicity and invertibility of the input-output map $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$

The results below show an influence of sign of the input Dirichlet data $u_0 > 0$ to the sign of the synthetic output data $\varphi_{ls} = (-D(x)u_x(x,t;D(x))_{x=0}$.

Lemma 5 *Let $D(x) \in L_\infty[0,L]$, and the solution of the forward problem (1) is continuously differentiable on the closure of Ω_T. If $u_0 > 0$, then $u_x(x,t) < 0, \forall (x,t) \in \Omega_T$.*

Proof Let $\psi(x,t) \in C_0^\infty(R^2)$ be an arbitrary smooth function with a compact support in Ω_T. Multiply the both sides of Eq. (1) by $\psi_x(x,t)$ and integrate by parts. Then we obtain:

$$\int_0^L (u\psi_x)|_{t=0}^{t=T} dx - \int\int_{\Omega_T} u\varphi_{xt} dxdt - \int_0^T (D(x)u_x\varphi_x)|_{x=0}^{x=L} dt + \int\int_{\Omega_T} D(x)u_x\varphi_{xx} dxdt = 0.$$

We apply integration by parts to the second integral:

$$\int_0^L (u\psi_x)|_{t=0}^{t=T} dx - \int_0^T (u\psi_t)|_{x=0}^{x=L} dt + \int\int_{\Omega_T} u_x\psi_t dxdt - \int_0^T (D(x)u_x\psi_x)|_{x=0}^{x=L} dt + \int\int_{\Omega_T} D(x)u_x\psi_{xx} dxdt = 0.$$

Hence

$$\int\int_{\Omega_T} (\psi_t + D(x)\psi_{xx})u_x dxdt = \int_0^T (u\psi_t)|_{x=0}^{x=L}\, dt + \int_0^T (D(x)u_x\psi_x)|_{x=0}^{x=L}\, dt - \int_0^L (u\psi_x)|_{t=0}^{t=T}\, dx. \tag{32}$$

Now we require that the function $\psi(x,t)$ is chosen to be the solution of the following backward parabolic problem

$$\begin{cases} \psi_t + D(x)\psi_{xx} = F(x,t), & (x,t) \in \Omega_T, \\ \psi(x,T) = 0, & x \in (0,L), \\ \psi(0,t) = 0, \quad \psi_x(L,t) = 0, & t \in (0,T). \end{cases} \tag{33}$$

Here $F(x,t)$ is an arbitrary continuous function $F(x,t)$ and will be defined below. Note that the backward parabolic problem (33) is well-posed, since replacing $t \in [0,T]$ by $\tau = T - t$ in the Eq. (33), the parabolic equation $\psi_\tau = D(x)\psi_{xx} - F(x, T-\tau)$ will be obtained.

Taking into account the initial and boundary conditions of (1) and (33) in (32), we get:

$$\iint_{\Omega_T} u_x(x,t)F(x,t)dxdt = -\int_0^T D(0)u_x(0,t)\psi_x(0,t)dt. \tag{34}$$

Now we apply the maximum principle to the adjoint problem (33). We require that the function $F(x,t)$ satisfies the condition $F(x,t) > 0$ on Ω_T. Then $\psi(x,t) < 0$ on Ω_T. This, with the boundary condition $\psi(0,t) = 0$, implies

$$\psi_x(0,t) := \lim_{h\to 0} \frac{\psi(h,t) - \psi(0,t)}{h} < 0, \quad \forall t \in (0,T].$$

Further, applying the maximum principle to the forward problem (1) and taking into account the condition $u_0 := u(0,t) > 0$, we conclude $u_0 > u(x,t) > 0, \forall (x,t) \in \Omega_T$. Therefore,

$$u_x(0,t) := \lim_{h\to 0} \frac{u(h,t) - u(0,t)}{h} < 0, \quad \forall t \in (0,T].$$

Hence the right hand side of (34) is negative, and we finally obtain:

$$\iint_{\Omega_T} u_x(x,t)F(x,t)dxdt < 0, \quad \forall F(x,t) > 0.$$

This implies the proof. □

Corollary 1 *Let conditions of Lemma 5 hold. Then the synthetic output data is positive:* $\varphi_{ls} = (-D(x)u_x(x,t;D(x))_{x=0} > 0, \forall t \in (0,T]$.

This result has a precise physical meaning. Assumption $u_0 > 0$ means that the initial concentration is positive. This physically means that the mass transfers from the surface of the electrode at $x = 0$, to the $x = L$, which means that the left flux is positive. This agrees with the assertion of the above Corollary 1.

The above lemma permits one to establish monotonicity of the input-output map $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$.

Theorem 1 *Let conditions of Lemma 5 hold. If the coefficients $D_1(x), D_2(x) \in \mathcal{D}$ satisfy the condition $D_1(x) \geq D_2(x), \forall x \in [0, L]$, then the output data $\varphi_{ls}^{(i)}(t)$, $i = 1, 2$, have the following property:*

$$\varphi_{ls}^{(1)}(t) := (-D_1(x)u_x(x, t; D_1(x))_{x=0} \leq$$
$$\varphi_{ls}^{(2)}(t) := (-D_2(x)u_x(x, t; D_2(x))_{x=0}, \qquad \forall t \in (0, T].$$

Proof For the given the coefficients $D_1(x), D_2(x) \in \mathcal{D}$ we use the integral identity (23) and the backward parabolic problem (24). Assuming the arbitrary function $p(t)$ in (24) positive, we can apply the Theorem 1 to the solutions $\psi(x, t)$ the backward parabolic problem (24), taking $p(t)$, instead of u_0. Then we obtain that $\psi_x(x, t)$ is positive on Ω_T. Further, Theorem 1 also implies that $u_{2x}(x, t) := u_x(x, t; D_2(x))$ is negative on Ω_T. Taking into account these results on the left hand side of the integral identity (23) we conclude that

$$\int_0^\tau p(t)\Delta\varphi_{ls}(t)dt \leq 0, \quad \forall \tau \in (0, T], \quad \forall p(t) > 0,$$

since $\Delta D(x) := D_1(x) - D_2(x) \geq 0$. This implies $\Delta\varphi_{ls}(t) := \varphi_{ls}^{(1)}(t) - \varphi_{ls}^{(2)}(t) \leq 0$. □

In particular we conclude from his theorem that the input-output map $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$ is well defined, since $\Delta D(x) = 0$ implies $\Delta\varphi_{ls}(t) = 0$.

Theorem 2 *If conditions of Theorem 1 hold, then input-output map $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$ is Lipschitz continuous, i.e.*

$$\|f_1 - f_2\|_0 \leq L_0\|k_1 - k_2\|_\infty \tag{35}$$

where $L_0 = \|u_{2x}\|_{H^0(\Omega_T)}\|\psi_x\|_{H^0(\Omega_T)}$

Proof Choosing the arbitrary function $p(t)$ in (24) as

$$p(t) = \frac{\varphi_{ls}^{(1)}(t) - \varphi_{ls}^{(2)}(t)}{\|\varphi_{ls}^{(1)} - \varphi_{ls}^{(2)}\|_{H^0[0,T]}}, \quad t \in (0, T],$$

and substituting it in (23) we get

$$\|\varphi_{ls}^{(1)} - \varphi_{ls}^{(2)}\|_{H[0,T]} \leq \|D_1 - D_2\|_\infty \int\int_{\Omega_\tau} u_{2x}\psi_x dxdt.$$

This implies the proof. □

The above results show the strict monotonicity and continuity of the input-output map $\Phi[\cdot] : \mathcal{D} \to \mathcal{F}$, which means existence and uniqueness of the solution of the inverse problem (1)–(2). However, the inverse problem (1)–(2) is severely ill-posed in the sense that small changes in the output data $\varphi_{ls}(t)$ do not correspond to small changes in the coefficient $D(x)$, as show the computational experiments given in the second part of the study.

5 Conclusion

The purpose of the paper was to demonstrate the feasibility of the adjoint problem approach to coefficient identification problem for pure diffusive linear model of chronoamperometry. The presented results allow to prove monotonicity, continuity, and hence invertibility of the input-output mappings $\Phi[\cdot] : K \to \mathcal{F}$ and $\Psi[\cdot] : K \to \mathcal{H}$. The integral identity relating solutions of the forward and corresponding adjoint problem plays an important tool in numerical implementation of the proposed approach. The presented in the second part of the study computational results show that the numerical algorithm based on integral identity (23) is permits one to reconstruct the unknown diffusion coefficient for the case of noise free and noisy measured output flux data.

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References

1. M. Ciszkowska, Z. Stojek, J. Electroanal. Chem. **466**, 129 (1999)
2. W. Kucza, M. Danielewski, A. Lewenstam, Electrochem. Commun. **8**, 416 (2002)
3. L.K. Bieniasz, Electrochem. Commun. **4**, 917 (2002)
4. J. Jammik, J. Maier, S. Pejovnik, Electrochem. Acta **44**, 4139 (1999)
5. J. Koryta, J. Dvořák, L. Kavan, *Principles of Electrochemistry*, 2nd edn. (Wiley, New York, 1993)
6. A. Hasanov, Ş. Hasanoglu, Math. Chem. **42**, 741 (2007)
7. Y. Jarny, N.M. Ozisik, J.P. Bardon, Int. J. Heat Mass Trans. **34**, 2911 (1991)
8. P. Knabner, S.J. Bitterlilich, Comp. Appl. Math. **147**, 153 (2002)
9. R. Nabakov, in *Parameter Identification and Inverse Problems in Hydrology, Geology and Ecology*. ed. by J. Gottlieb, P. DuChateau (Kliver Academic Publishers, Netherland, 1996), p. 155
10. M. Hanke, O. Scherzer, SIAM J. Appl. Math. **59**, 1012 (1999)
11. D.E. Reeve, M. Spivack, J. Comput. Phys. **151**, 585 (1999)
12. G.R. Richter, Math. Comput. **36**, 375 (1981)
13. P. DuChateau, SIAM J. Math. Anal. **28**, 611 (1997)
14. A. Hasanov, P. DuChateau, B. Pektaş, J. Inv. Ill-Posed Prob. **14**, 435 (2006)
15. P. DuChateau, R. Thelwell, G. Butters, Inverse Probl. **20**, 601 (2004)
16. L.C. Evans, *Partial Differential Equations* (American Mathematical Society, Providence, 1998)
17. V.K. Ivanov, V.V. Vasin, V.P. Tanana, *Theory of Linear Ill-Posed Problems and its Applications* (Nauka, Moscow, 1978)
18. A. Hasanov, J. Math. Anal. Appl. **330**, 766 (2007)