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Boundary Control of Reacting Species in Semi-infinite and Finite Diffusion Processes

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Abstract: Boundary control of oxidizing species at the cathode surface is considered in an electrochemical system, which is the plant of two electrodes and plant of three electrodes submerged in the stirred and unstirred electrolytes. The exact feedforward controls are found using ideas of motion planning, Laplace transform and other techniques that in the end solve the inverse problem for the given time-variable reference of species at the cathode surface. The uncertainty of surface reaction existing in the system is suppressed with two modifications of controls. In the first case, the feedforward control is extended with a PI feedback that uses measured in the process electric current passing through the system. In the second case, an adaptive feedforward control is established for the case when the exchange current density is unknown drifting parameter and is estimated as it changes using a conditionally Gaussian filter. In both cases, the process control is simulated and revealed to be effective.

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1. Introduction

The problem solved in this paper stems from an industrial plating process, where the production maximization is crucial. This is closely related to the plating rate maximization and this in turn means maximization of the current density. However, a substantial rise of the current density ends up with depletion of the oxidizing species at the cathode surface which leads to a reduced plating rate and production. Therefore, reactant concentration control is a close objective that helps to avoid the depletion while maximizing the current density through stabilization of the boundary concentration at a wisely chosen reference profile. The concentration control is a transient control problem. It aims to bring the concentration at the boundary from a bulk solution concentration to a prescribed level in a completely controlled manner.

2. The problem statements

General electrodeposition obeys convection, migration and diffusion laws. However, when observing the mass-transfer effects close to an electrode surface, the diffusion does prevail. For that reason, concentration of reacting species is modelled by a diffusion equation:

$$-D \partial_t c(t,x) = D \partial_x^2 c(t,x).$$

The initial distribution of species is assumed to be homogeneous in the stagnation layer and equal to the bulk solution concentration:

$$c(0,x) = c_{\text{bulk}}.$$

The condition on the cathode is given by the first Fick law and states that the molar flux of reacting species is proportional to the cathode current density:

$$-D \partial_t c(t,x)|_{t=0} = \frac{i(t)}{nF}.$$

In the case of unstirred electrolytes (semi-infinite diffusion), the condition at the outer boundary is given as the concentration in bulk solution

$$c(t,\delta) = c_{\text{bulk}}.$$

In well agitated electrolyte a finite diffusion takes place within a certain thickness $\delta$ of the stagnation layer. In such a case the inner boundary condition remains the same, while the outer boundary is immobile (fixed spatially condition)

$$c(t,\delta) = c_{\text{bulk}}.$$

In (1)-(4), $c(t,x)$ is the concentration (mol/m$^3$) of species in the depth $x$ of the stagnation layer (m), $c_{\text{bulk}}$ is the bulk solution concentration (mol/m$^3$), $D$ is the diffusivity (m$^2$/s), $F$ is the Faraday constant (96485 C/mol), $n$ is the number of electrons involved in an electrode reaction and $i(t)$ is the current density (A/m$^2$) of an electrode reaction that satisfies a bidirectional Butler-Volmer (B-V) equation [1, 2]

$$i(t) = i_0 \left( e^{(1-\alpha)E(t)} - e^{\alpha E(t)} \right).$$

In (5), $i_0$ is the exchange current density (A/m$^2$), $\alpha$ is the apparent transfer coefficient and $k$ is the temperature voltage ($V^{-1}$). The mass-transfer effect is considered through including the concentration of oxidizing species near the electrode surface $c(t,0)$ in the model (5). $E(t)$ is the voltage applied to an electrochemical system (V), considered as the control. In two-electrode plant, the applied voltage is the difference between anodic and cathodic overpotentials each of them is once more difference between the electrode potential and equilibrium potential. The equilibrium potential $U(t)$ can be measured in practice with respect to a reference electrode (versus SHE).
that is submerged in electrolyte at the cathode surface in the
case of three-electrode system. The device shown in Fig 1 is
used for the boundary concentration \(c(t,0)\) evaluation from
the indirect measurement \(U(t)\). The evaluation procedure is
explained later in subsection 4.1, where the Nernst relationship
(25) and its inverted stochastic modification (26) are introduced.

\[
U(t) \quad E(t)
\]

Fig. 1. Scheme and apparatus of three-electrode measurements.

We are seeking for a control that brings the concentration at
the boundary from the bulk solution concentration \(c_{\text{bulk}}\) to a
lower level \(c_{\text{min}}\) near the cathode surface in a fully controlled
manner. The prescribed reference is set by a time-varying
function that declines exponentially

\[
c_{\text{ref}}(t) = c_{\text{min}} + (c_{\text{bulk}} - c_{\text{min}}) e^{-\gamma t}.
\]

(6)

Here \(c_{\text{ref}}\) is the reference trajectory of the concentration at the
boundary, \(c_{\text{min}}\) and \(\gamma\) are the positive-valued constants, that
specify the desired concentration at the boundary at steady
state and the rate of tracking to steady state respectively. We
are not concerned with the question of choosing \(c_{\text{min}}\) and \(\gamma\).
In this paper, we will focus on the development of a control law
to follow the reference trajectory (6).

3. Motion planning

The problem of designing a voltage \(E(t)\), which is to be
applied to (1)-(5) forces the concentration at the boundary to
follow a given reference trajectory, is a boundary control
problem known also as a motion planning problem [3].

To solve the motion planning problem one should find a
reference profile \(c_{\text{ref}}(t,x)\) in the whole subdomain of the
stagnation layer. This profile can be found by replacing in (1)-(4)
the boundary condition (3) with

\[
c(t,0) = c_{\text{ref}}(t).
\]

(7)

The motion planning problem is solved further in the case of
semi-infinite diffusion and finite-length diffusion processes
for the reference trajectory given by (6).

3.1 Semi-infinite diffusion

Perhaps, the simplest way to discovery the reference
trajectory in the whole subdomain in the case of semi-infinite
diffusion is to apply the Laplace transform to the diffusion
equation (1) with the Dirichlet boundary conditions (7) and
(4a). This transform reduces the diffusion equation (1) into a
solvable ordinary differential equation. Incorporating the
corresponding boundary conditions yields the solution in a
complex argument variable \(S\)

\[
c_{\text{ref}}(S,x) = \left(c_{\text{bulk}} - c_{\text{min}} \right) \left(\frac{1}{S + \gamma} \right) e^{-\sqrt{D} \frac{S}{S + \gamma}} + \frac{c_{\text{bulk}}}{S}.
\]

(8)

Here \(c_{\text{ref}}(S,x)\) is the Laplace transform of \(c_{\text{ref}}(t,x)\) and the
subscript \(\text{ref}\) indicates correspondence to the target profile.
Equation (8) is the solution of motion planning problem in the
Laplace domain for the model (1)-(3) and the reference
concentration (6) at the boundary (7). The controller can be
derived without the analytical inverse transformation of (8) in
the whole subdomain but on the controlled boundary. Indeed,
according to the Neumann boundary condition (3) the
controller is governed by the flux of species at the boundary.
Differentially \(c_{\text{ref}}(S,x)\) with respect to \(x\) and taking controlled
boundary \(x = 0\), yields

\[
\partial_x c_{\text{ref}}(S,x) \bigg|_0 = \frac{c_{\text{bulk}} - c_{\text{min}}}{\sqrt{D}} \left(1 - \sqrt{\frac{S}{S + \gamma}} \right).
\]

(9)

The solution in time domain can be found as the inverse
Laplace transforms of (9)

\[
\partial_x c_{\text{ref}}(t,x) \bigg|_0 = -\frac{\gamma}{\sqrt{D}} \left(c_{\text{bulk}} - c_{\text{min}}\right) e^{-\gamma t} \text{erf} \left(j \sqrt{\gamma t} \right).
\]

(10)

In (10), symbol \(j\) stands for the imaginary unit. It is known
that \(\text{erf}(jz) = -\text{erfi}(z)\) for any complex argument \(z\) [4],
where the function \(\text{erfi}\) is the imaginary error function
defined as

\[
\text{erfi}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^x^2 \, dx.
\]

(11)

Consequently, taking real value \(z = \sqrt{\gamma t} + j0\) the desired flux
at the boundary can be written in the terms of the imaginary
error function as

\[
\partial_x c_{\text{ref}}(t,x) \bigg|_0 = \frac{\gamma}{\sqrt{D}} \left(c_{\text{bulk}} - c_{\text{min}}\right) e^{-\gamma t} \text{erfi} \left(\sqrt{\gamma t} \right).
\]

(12)

In contrast to the error function, the imaginary error function
rapidly diverges to infinity as \(z\) grows. However, the function
\(F(z) = e^{-z^2} \text{erfi}(z)\) is bounded for all real \(z\)-values.

To find the boundary control the boundary condition (3)
can be utilized. In the tracking mode the flux at the boundary
also obeys the first Fick law

\[
-D \partial_x c_{\text{ref}}(t,x) \bigg|_0 = \frac{i_{\text{ref}}(t)}{n_F},
\]

(13)

where \(i_{\text{ref}}(t)\) is the current density corresponding to the desired
reference concentration. Assuming the bidirectional electrode
model (5)

\[
i_{\text{ref}}(t) = i_0 \left( e^{-(1-\alpha) t} c_{\text{ref}}(t) - \frac{c_{\text{ref}}(t)}{c_{\text{bulk}}} e^{-\alpha t} c_{\text{ref}}(t) \right),
\]

(14)

the tracking control can be found as follows. Define a function
\[ y = e^{ax} - ce^{-bx} = f(x; a, b, c). \]  
(15)

In this definition, \( a \) and \( b \) are the arbitrary nonnegative constants and \( c \) is the strictly positive. The latter function is invertible, partly \( 2f^{-1}(y; 1,1,1) = arsinh(y) \), generally inverse is a continuous bounded function, denoted by

\[ x = f^{-1}(y; a, b, c). \]  
(16)

Given \( y, a, b, \) and \( c \), the inverse function above can be fast computed using the bisection method, Newton’s method or other simple method. The control, that forces the concentration at the boundary to follow the prescribed reference trajectory is the continuous bounded function \( (17) \).

\[ E_{ref}(t) = f^{-1} \left( \frac{-nF \sqrt{D} \gamma}{l_0} (c_{bulk} - c_{min}) e^{-\gamma t} erf\left(\sqrt{\gamma t}\right) \right) \]  
(17)

### 3.2 Finite-length diffusion

Like that of semi-infinite diffusion, we calculate the reference profile \( c_{ref}(t,x) \) inside the whole subdomain from the diffusion equation \( (1), (2) \) with the Dirichlet boundary conditions \( (7) \) and \( (4b) \). Using a new variable

\[ w(t, x) = c_{ref}(t,x) - c_{ref}(t) - \delta^{-1} x (c_{bulk} - c_{ref}(t)), \]  
(18)

one can lift the boundary data to homogeneous boundary that contributes a result: a source-like term

\[ R(t, x) = ye^{-\gamma t} \left( c_{bulk} - c_{min} \right) \left(1 - \delta^{-1} x \right) \]  
(19)

in the diffusion equation

\[ \partial_t w(t, x) = D\partial_x^2 w(t, x) + R(t, x), \]  
(20)

With the zero initial condition \( w(0, x) = 0 \) and the homogeneous boundary conditions \( w(t, 0) = 0 \) and \( w(t, \delta) = 0 \). This problem can be solved analytically using the separation of the variables method. This eventually yields the following solution

\[ w(t, x) = 2y \frac{c_{bulk} - c_{min}}{\delta} \sum_{n=1}^{\infty} \lambda_n \left( \lambda_n^2 D - \gamma \right) \sin\left(\lambda_n x\right), \quad \lambda_n = \frac{n\pi}{\delta}. \]  
(21)

Using (21), the reference profile given as the solution of the original problem can be expressed as

\[ c_{ref}(t, x) = w(t, x) + c_{ref}(t) + \delta^{-1} x \left( c_{bulk} - c_{ref}(t) \right). \]  

Consequently, the flux at the boundary is given by

\[ \partial_x c_{ref}(t, x)|_b = \frac{c_{bulk} - c_{min}}{\delta} \left( 1 - e^{-\gamma t} + 2y \sum_{n=1}^{\infty} \frac{e^{-\lambda_n^2 \delta t}}{\lambda_n^2 D - \gamma} \right). \]  
(22)

Once again to develop the boundary control, the inner boundary condition \( (3) \) is utilized. In the tracking mode, the flux at the boundary satisfies the first Fick law \( (13) \). Assuming the bidirectional model \( (14) \) leads to the following boundary control

\[ E_{ref}(t) = f^{-1} \left( \frac{-nF \sqrt{D} \gamma}{l_0} (c_{bulk} - c_{min}) x \right) \]  
(23)

The control system. The structure of the control system developed for maintenance of the concentration of species at the tracking reference at the boundary is depicted in Fig. 2.

Fig. 2. The feedforward control system. This represents the motion planed control for maintenance of the boundary concentration at given target.

The designed feedforward boundary controllers \( (17) \) and \( (23) \) do not tolerate extensive uncertainties. To deal with uncertainties (unmodeled convection, migration and other effects) they should be accompanied with a feedback.

### 4. Uncertain system control

Effective use of the feedforward controls \( (17) \) and \( (23) \) requires a good knowledge of the model, which is not the case. Usually, the model is known poorly and is more complex. For that reason, the deterministic controls are modified below with a feedback from measured in the process data and with adjustment of the model to unknown stochastic drift.

#### 4.1 PI modified feedforward control

The feedforward controls \( (17) \) and \( (23) \) can be improved with a simple feedback, if instead of \( c_{ref}(t) \) its PI modified values \( c_f(t) \) are used

\[ c_f(t) = K_p \left( c_{ref}(t) - \zeta(t) \right) + \frac{1}{T_i} \int_0^t \left( c_{ref}(s) - \zeta(s) \right) ds \]  
(24)

In (24), \( \zeta(t) \) is the measured concentration at the boundary (mol/m³), \( K_p \) is the regulator gain, and \( T_i \) is the integral time (s). The concentration \( c(t, 0) \) at the boundary can be measured indirectly as the potential \( U(t) \) or voltage between electrodes in a three electrodes system [1]. This voltage and concentration are related to each other as shown below in the Nernst relationship

\[ U(t) = U_{eq} + \frac{1}{k} \ln \left( \frac{c(t, 0)}{c_{bulk}} \right). \]  
(25)
Here $U(t)$ is the electrode potential and $U_{eq}$ is the equilibrium potential measured versus a reference electrode [1].

If the equation (25) is inverted (solved with respect to the concentration) and additive white noise error is added, which is more relevant to the real case, the measurement signal can be expressed as in (26).

$$
\xi(t) = c_{\text{bulk}} e^{(t-U_{eq})/c_{\text{ref}}} + r \xi(t)
$$

(26)

Here $\xi$ is the measured indirectly boundary concentration, $r$ is the independently distributed standard Gaussian variable of zero mean and unit variance $r \sim N(0,1)$, and $r$ is the accuracy of measurements.

**The feedback control system.** The structure of the control system developed for uncertain model for maintenance of the concentration of species at the tracking reference at the boundary is depicted in Fig. 3. The feedforward controller is extended with the PI-feedback. This system obliges three-electrode measurements to be implemented.

![Fig. 3. The feedback modified feedforward control system.](image)

**4.2 Adaptive control: unknown stochastic drift**

To deal with the uncertainties of electrode kinetics an adaptive control can be applied. One can use the certainty equivalent approach that replaces the unknown parameters with their estimates in the control laws (17) and (23) or cautious controls applied that uses variance of the estimates as well (applied in this paper).

The exchange current density $i_0$ and apparent transfer coefficient $\alpha$ are usually poorly known as well as the diffusivity coefficient $D$. The model is nonlinear by the latter two parameters. They can be estimated from a relatively complex Zakai equation [5, 6]. The model is linear by the exchange current density $i_0$, we assume that it changes in time as a linear stochastic process $\theta(t)$:

$$
d\theta = (a_0 + a_1 \theta(t)) dt + \sigma \epsilon(t), \quad \theta(0) = \theta_0
$$

(27)

with a partly unknown initial condition $\theta_0 \sim N(m_0, \gamma_0)$ - specified by a Gaussian distribution with a given mean $m_0$ and covariance $\gamma_0$. They serve for initial guess. In (27), $a_0$, $a_1$ are the parameters specifying dynamics of the process, $\sigma$ is the parameter specifying other effects of unmodeled kinetics along with a Wiener process $W$.

The measured current density $m(t)$ (of (25) can be rewritten in terms of the drifting $\theta(t)$ exchange current density $i_0$ and measurement errors, as

$$
\xi(t) = A_1 \theta(t) + BV(t),
$$

(28)

where $\xi$ is the measure current density $(A/m^2)$, $B$ is a given parameter that specifies accuracy of the measurements, $V$ is a generalized white noise that can be expressed as another Wiener process $V$ in Ito integral and $A_1$ is the time-varying function specified by (5) as

$$
A_1 = e^{(t-U_{eq})/c_{\text{ref}}} - e^{-k(1-\alpha)} c_{\text{bulk}} e^{(t-U_{eq})/c_{\text{ref}}}.
$$

(29)

In the case of three-electrode system the boundary concentration can be found from the Nernst equation and if replaced in (29) gives

$$
A_1 = e^{(t-U_{eq})/c_{\text{ref}}} - e^{-k(1-\alpha)} c_{\text{bulk}} e^{(t-U_{eq})/c_{\text{ref}}}.
$$

(30)

The unknown drift of the exchange current density can be estimated from the measured data using the best mean-square filter [7] specified for the system (27) and (28):

$$
dm(t) = (a_0 + a_1 m(t)) dt + A_1 \gamma_1 (dy - A_1 m(t) dt), \quad m(0) = m_0,
$$

(31)

where $m_i$ is the conditional mean $m_i = M_{i_0(t)} f_i^\gamma$ of the unknown drift and $\gamma_1$ is the mean variance (accuracy)

$$
\frac{dy}{dt} = 2a_1 \gamma_1 + b^2 - A_1^2 \frac{\gamma_1^2}{b^2}, \quad \gamma(0) = \gamma_0.
$$

(32)

To avoid the potential problems like division by zero in implementation of (17) and (23) while the estimate $m$ is applied instead of $i_0$, the inverse of the exchange current density is approximated by

$$
i_0^{-1} = i_0/\sqrt{i_0 + \eta},
$$

(33)

where $\eta$ is a small parameter $\eta > 0$. The mathematical expectation of the concave function (33) is upper-bounded with the function of mean and variance

$$
M_{i_0} \leq \frac{m}{i_0 + \eta}.
$$

(34)

Alternatively, a more complex exact expectation can be expressed through the imaginary part of the complex argument probability function $\omega(z) = e^{-z^2} \text{erfc}(-jz)$ as follows

$$
M \leq \frac{i_0}{i_0 + \eta} = \frac{1}{\gamma} \sqrt{\frac{\pi}{2}} \text{Im} \omega(z), \quad z = \frac{m^2}{\gamma} + j \frac{\eta}{\gamma}.
$$

(35)

According to the cautious control approach the hyperbolic function of unknown exchange current density in (17) and (23) is replaced by its upper-bounded function (33) estimate (34) (alternatively estimate (35)), which leads to the controls

$$
E_{ref}(t) = f^{-1} \left[ -nF \sqrt{D}\gamma \left( c_{\text{bulk}} - c_{\text{min}} \right) e^{\gamma t} \text{erfi} \left( \sqrt{\gamma t} \right); \begin{cases}
\frac{k(l-\alpha)}{k(l-\alpha)}, k\alpha, \frac{c_{\text{ref}}(t)}{c_{\text{bulk}}}
\end{cases} \right]
$$

(36)
for the semi-infinite diffusion process, and

$$E_{ref}(t) = f^{-1}\left(1-e^{-\gamma t} + 2\sum_{n=1}^N e^{-\gamma t} - e^{-2\gamma t}\right);$$

(37)

for the finite-length diffusion process.

The adaptive control system. The structure of the adaptive control system developed for tracking of the drift and for maintenance of the concentration of species at the tracking reference at the boundary is depicted in Fig. 4. This feedforward controller is adaptive to unknown stochastic 3drift. This system oblige three-electrode system measurements to be implemented.

In a two-electrode system the Nernst inverted part is missing in Fig. 4. In this case, the boundary concentration required in (29) should be found from solved diffusion model as explained below.

4.3 The boundary concentration solved using model

The semi-infinite diffusion. The boundary concentration can be evaluated by past current density measurements, if the current density is replaced with measurements in the analytical solution (38) found for the semi-infinite diffusion problem with Laplace method

$$c(t,0) = c_{bulk} + \frac{1}{nF\sqrt{\pi D}} \int_0^\infty \frac{i(\tau)}{\sqrt{t-\tau}} d\tau.$$  

(38)

Following Nicholson and Shain [8], the convolution integral in (38) can be approximated as

$$\int_0^\infty \frac{i(\tau)}{\sqrt{t-\tau}} d\tau \approx 2\sqrt{h} \sum_{k=1}^N i(kh) \left(\sqrt{n-k+1} - \sqrt{n-k}\right),$$

(39)

where $N$ is the number of samples and $h$ is the discretization step (s). Replacing in the equation (39) the modelled current density with the measured current density gives the desired estimate of the concentration at the boundary:

$$c(t,0) \approx c_{bulk} + \frac{2}{nF} \sqrt{\frac{h}{\pi D}} \sum_{k=1}^N \xi(kh) \left(\sqrt{n-k+1} - \sqrt{n-k}\right).$$

(40)

The finite-diffusion. The concentration estimate at the boundary for the finite-length diffusion can be found similarly from the analytical solution by replacement of $i(\tau)$ with measurements $\xi(\tau)$ in another convolution-like solution of [7]

$$c(t,0) = c_{bulk} + \frac{1}{nF\sqrt{\pi D}} \int_0^\infty \frac{\xi(\tau)}{\sqrt{t-\tau}} d\tau.$$  

(41)

where $\xi$ is the measured current density (A/m$^2$).

5. Control simulation

The control effect was tested in simulation. The reaction occurring at the electrode was assumed to be a single step reaction with two exchanged electrons ($n = 2$). The values of kinetic and mass-transfer parameters utilized in the simulation are listed in Table 1.

![Table 1](image)

TABLE I  

| Symbol | QUANTITY | Value |
|--------|----------|-------|
| $i_0$  | Exchange current density (mean) | $42 \text{ A/m}^2$ |
| $\alpha$ | Apparent transfer coefficient | $0.25$ |
| $D$ | Diffusivity | $4 \times 10^{-9} \text{ m}^2/\text{s}$ |

The semi-infinite diffusion. The semi-infinite diffusion process at the boundary was simulated as (38) along with the concentration measurements (16) and then controlled by the PI modified feedforward controller (24) that forces the concentration at the boundary to follow the reference trajectory (6) with $c_{min} = 100 \text{ mol/m}^3$, $c_{bulk} = 750 \text{ mol/m}^3$ and $\gamma = 1$. The measurement accuracy (standard deviation) of concentration at the boundary was assumed to be $r = 5 \text{ mol/m}^3$. The PI controller parameters $K_p = 4$ and $T_i = 100$ were selected from the best performance of the simulation. The tracking of the boundary concentrations with such a controller is illustrated in Fig. 5 as well as the tracking errors and control signals in Figs 5 and 6 respectively.

![Figure 5](image)  

Fig. 5. The concentration tracking at the boundary.
The finite-diffusion. The finite-diffusion process was simulated along with the measured (28) and controlled by adaptive controller (37) that forces the concentration at the boundary to follow the reference trajectory (6). The exchange current density $i_0$ was assumed to be an unmeasured stochastic process (27) with the known mean: $-\alpha_0/\alpha_1 = 42$, dynamics $\alpha_1 = -1$ and standard deviation $b = 3$ of noise. This process started in simulation from the initial value $i_0(0) = 50$. The measurement accuracy (standard deviation) of the current density measurements was assumed to be $B = 10$ A/m$^2$. Calculation by the filter (31), (32) started from the guess values $m_0 = 100$ and $\gamma_0 = 400$. The concentration tracking error of simulation is illustrated in Fig. 8 and the exchange current density estimated in Fig. 9. The tracking error is shown in two cases when the drifting parameter is known and when it is estimated from the electric current measurements.

6. Conclusion

This study has shown that the feedforward controllers for the semi-infinite diffusion and finite-length diffusion processes nonlinear at the boundary can be derived in the form of semi-explicit control function. These controllers, if modified, can deal with uncertainties and unmodeled dynamics. The effectiveness of the proposed controls is verified by means of simulations.

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