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Modeling of galvanostatic pulse and pulsed reverse electroplating of gold

Zhengwei Liu*, Alan C. West

Department of Chemical Engineering, Columbia University, NY 10027, United States

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1. Introduction

Hard gold, obtained from electroplating of gold with cobalt or nickel, has been widely used as an electrical contact material because of its electrical and mechanical properties [1]. Because of its high costs, it is desirable to reduce the thickness of gold contact layers. However, the gold layer cannot be too thin because deposit porosity may lead to corrosion of the underlayer, leading to contact failures [2]. Porosity (as observed by scanning electron microscopy in a recent study [3]) was linked to the microstructure of the deposit and also the rate of the hydrogen evolution reaction. In was found [3,4] that both on–off pulse plating and pulse-reverse plating can result in deposits with lower porosity. Because the parameter space required to optimize the plating process is large, simulations have been developed as a tool for waveform development. These simulations can predict time–average current efficiency, one of the key factors impacting porosity.

Previously, a diffusion model has been developed by Cheh [5,6] to calculate the gold deposition rate by pulse and pulsed reverse plating. Simulations effectively predict the limiting current density for DC and pulse plating conditions in various electrolytes, including a cyanide bath that is similar to the one of interest to this study. Since this model did not attempt to explicitly account for side reactions such as hydrogen evolution or the complex nature of the anodic dissolution reaction [7], it was not necessary to model in detail the electrode kinetics. For conditions of relevance to indus-

ABSTRACT

A mathematical model of galvanostatic pulse and pulsed reverse electroplating of gold on a rotating disk electrode is presented. Using experimental polarization curves, dc current efficiencies, and literature-reported diffusion coefficients, model parameters are estimated. An accurate prediction of current efficiency by the on-off pulse-plating model was confirmed by experimental measurement. The current efficiency of pulse-reverse plating at relatively low waveform frequency is also successfully predicted, with less agreement at higher frequencies, presumably due to the simplified approach that the model employs to treat the complex set of reactions that occur during the anodic portion of the wave. When the reduction of adsorbed gold species produced during the oxidation portion of the pulse is included, improved agreement between experiment and theory is obtained.

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trial gold contact plating, the hydrogen evolution reaction may consume more than 40% [8,9] of the current, with a precise value depending on the particular bath and plating rate. Several experimental but no simulation studies of hydrogen evolution [10,11] have been conducted for gold plating systems.

In the pulsed reverse plating study, Cheh [6] suggested that the amount of near-surface cyanide, released when gold is reduced, may be too low to allow for significant gold dissolution during current reversal We have recently used a quartz crystal microbalance [7] to quantify the amount of soluble gold that produced. To the best of our knowledge, simulations have not been developed to address the complex processes that may occur during pulse reversal.

In this paper, we develop a model that predicts the behavior of the gold-cyanide plating system during pulse and pulsed reverse plating. Using experimental polarization curves, dc current efficiencies, and literature-reported diffusion coefficients, model parameters are estimated. Similar models has been developed and utilized in other metal or alloy plating systems, such as Cu [12], CuNi alloy dc plating [13] and pulse plating [14,15], Mo alloys [16,17], Fe group metals [18], and giant magnetoresistance multilayers [19].

2. Experimental

The experimental details of cobalt hard gold electroplating were described previously [3,7]. The gold plating bath, with a commercial name of Metalor Gold, from Metalor Technology, contains 0.04 M KAu(CN)₂, cobalt additives (approximately 0.008 M in solution, resulting in around 0.5 wt.% of Co in the electrodeposits) and supporting electrolyte including: conducting salt (a mixture of organic acid salt and potassium oxalate monohydrate), acid salt

^{*} Corresponding author. E-mail address: liuzhengw@gmail.com (Z. Liu).

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Nomenclature						
List of sy	List of symbols					
<i>c</i> _{Au}	concentration of Au(CN) ₂ ⁻ , mol cm ⁻³					
c _{HCN}	concentration of HCN, mol cm ⁻³					
<i>C</i> _{<i>i</i>.0}	bulk concentration of Au or HCN, mol cm ⁻³					
$C_{i,s}$	surface concentration of Au or HCN, mol cm ⁻³					
E	applied potential, V vs. Ag/AgCl reference					
F	Faraday's constant, 96,487 equiv mol ⁻¹					
i _{Au}	Au current density of gold reduction or dissolution					
	$mA cm^{-2}$					
i _{ads}	current density of AuCNads layer formation,					
	$mA cm^{-2}$					
i _{avg}	average current density, mA cm ⁻²					
i _H	current density of hydrogen evolution, mA cm ⁻²					
<i>i</i> 02	i_{O_2} current density of oxygen evolution, mA cm ⁻²					
i _{on}	cathodic current density, mA cm ⁻²					
<i>i</i> _{rev}	anodic current density, mA cm ⁻²					
R	universal gas constant, 8.314 J/mol K					
ton	length of on time, s					
toff	length of off time, s					
t _{rev}	length of reversal time, s					
Т	temperature K					
Creek						
QA.	cathodic transfer coefficient of gold reduction					
Qu	cathodic transfer coefficient of bydrogen evolution					
$\Omega^{\alpha_{\Pi}}$	resistance of plating electrolyte $ohm^{-1}cm^{-1}$					
Γ	the areal density of a monolayer, mol cm^{-2}					
θ	surface coverage of AuCN _{ade} laver					
ω	rotation rate rad s ⁻¹					
υ	kinematic viscosity of solution, cm ² s ⁻¹					

(citrate based), and brightener (mixture of potassium hydroxide and aromatic compounds). The pH of this bath was 5 at room temperature. The temperature of the plating bath was set to 45 °C using a water bath (Isotemp 3016 Fisher Scientific). All plating work was conducted on a 1 mm Cu RDE at rotation rate of 2500 rpm. A rectangular waveform, including pulse and pulsed reverse plating, was used. Current efficiency was evaluated by the coulometric stripping method [5]. The QCM measurements were performed using 5 MHz polished Ti/Au crystals (Maxtek) with a Maxtek Research Quartz Crystal Microbalance (RQCM, MCD 260).

3. Model development

Gold plating from a cyanide bath is modeled. Cobalt is added in the electrolytes as a grain refiner and present in the electrodeposit with a low content, commonly less than 0.5% [20]. Due to its low content, in the model we neglect the cobalt reduction and oxidation currents. The impact of the multiple additives and cobalt is neglected. While these may be important, the model captures the salient features of the presently reported experimental measurements. The model was fit to polarization curves obtained from plating in this complete bath, and thus the additives and cobalt are only implicitly considered. Further model refinements, including a more exhaustive treatment of bath chemistry and the electrode kinetics, are warranted. For comparison with experiment, the bulk concentration of gold-cyanide was set to 0.04 M. The bulk excess cyanide concentration was also set to zero for all simulations, since the high stability constant of gold-cyanide constant, from Ref. [21], gives a equilibrium excess cyanide concentration of $4\times 10^{-17}\,\text{M}.$

One-dimensional mass transfer to a rotating disk electrode (RDE) is considered. The concentration of each species is given by:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \tag{1}$$

where *R_i* is the homogeneous reaction rate. The flux term *N_i* is given as

$$N_{i} = -\frac{z_{i}D_{i}Fc_{i}}{RT}\frac{\partial\Phi}{\partial x} - D_{i}\frac{\partial c_{i}}{\partial x} + \nu_{x}c_{i}$$
⁽²⁾

where the electromigration term in Eq. (2) is small and can be neglected when excess supporting electrolyte is present [22].

Several homogeneous reactions, including citric-acid dissociation reactions, hydrogen–cyanide dissociation reactions, as well as water dissociation, are known to be important. We assume all the chemical homogeneous reactions are at equilibrium. Based on a speciation analysis using well-established equilibrium constants, the model is simplified by solving for the concentrations c_{Au} and c_{HCN} of the two dominant species at the electrolyte pH of 5: Au(CN)₂⁻ and HCN. The electrolyte is strongly buffered, and we further assume that the electrolyte pH is invariant, even though hydrogen evolution is an important side reaction.

With the above simplifications, the governing equation can be written as

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - \nu_x \frac{\partial c_i}{\partial x}$$
(3)

where D_i is the diffusion coefficient of species *i* (for Au(CN)₂⁻ and HCN) and ν_x is the axial velocity, given by $\nu_x = -0.51023 \,\omega^{2/3} \nu^{-1/2} x^2$ near the electrode surface [23].

Two reactions are assumed during the reduction portion of the pulsed waveform:

$$Au(CN)_2^- + 2H^+ + e^- \rightarrow Au + 2HCN$$
(4)

and

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (5)

The rate of reaction (4), assuming relatively high overpotentials, is given by a Tafel equation, with first order kinetics [9,24–27]:

$$i_{Au} = -k_{Au} \exp\left[\frac{-\alpha_{Au}F}{RT}(E-i\,\Omega)\right]c_{Au}$$
(6)

and the hydrogen evolution reaction is given by:

$$i_{\rm H} = -k_{\rm H} \, \exp\left[\frac{-\alpha_{\rm H}F}{RT}(E - i\,\Omega)\right] \tag{7}$$

From reaction (4), the electrode boundary conditions for the flux of $Au(CN)_2^-$ and HCN are given by Faraday's law:

$$-D_{Au}\frac{\partial c_{Au}}{\partial x} = \frac{D_{HCN}}{2}\frac{\partial c_{HCN}}{\partial x} = \frac{i_{Au}}{F}$$
(8)

The total applied current is given by

$$i_{\rm on} = i_{\rm Au} + i_{\rm H} \tag{9}$$

where double layer charging is neglected [28]. During the off time in pulse plating, we assumed:

$$i_{\rm Au} = i_{\rm H} = 0 \tag{10}$$

During the reverse time in pulsed reverse plating, at least three oxidation reactions may occur [7]:

(1) Soluble gold is initially produced until near-surface excess cyanide (c_{HCN}) is consumed:

$$Au + 2HCN \rightarrow Au(CN)_2^- + e^- + 2H^+$$
(11)

(2) then an adsorbed gold cyanide layer, involving $Au(CN)_2^-$ from the electrolyte, is formed

$$Au + Au(CN)_2^- \rightarrow 2AuCN_{ads} + e^-$$
(12)

(3) and complex gold oxidation reactions, forming trivalent gold, may also happen, as well as the oxygen evolution reaction. The rate of this reaction is denoted i_{0_2} .

Based on these reactions, two limiting models were developed. In Model 1, it is assumed that when the surface concentration of excess cyanide is greater than zero

$$i_{Au} = i_{rev} \quad \text{when} \, c_{HCN} > 0 \tag{13}$$

and when the excess cyanide is depleted,

$$\iota_{O_2} = \iota_{rev} \tag{14}$$

In Model 2, which was created to obtain better agreement with experimental results, the adsorbed gold cyanide layer is introduced. We assume Eq. (13) when $c_{HCN} > 0$. Following depletion of the nearelectrode HCN, the gold is oxidized according to reaction (12) until a monolayer of AuCN is formed:

$$i_{ads} = i_{rev} \quad when \theta < 1$$
 (15)

where the amount of adsorbed AuCN is given by a material balance:

$$\Gamma \frac{\partial \theta}{\partial t} = \frac{2i_{\text{ads}}}{F} \tag{16}$$

where the areal density of a monolayer Γ is assumed to be $2 \times 10^{-9} \text{ mol cm}^{-2}$ if the gold is atomically smooth. After a monolayer of AuCN_{ads} is formed (θ = 1), Eq. (14) is assumed to apply. In both Models 1 and 2, Faraday's law is applied to relate the flux of the soluble gold cyanide species and HCN to the reverse current.

When Model 2 is used, the on-time boundary condition is further modified by assuming that the adsorbed layer is first reduced at 100% current efficiency when $\theta > 0$:

$$H^{+} + AuCN_{ads} + e^{-} \rightarrow Au + HCN$$
(17)

During this time,

$$\frac{\partial c_{Au}}{\partial x} = 0$$
 and $D_{HCN} \frac{\partial c_{HCN}}{\partial x} = \frac{i_{on}}{F}$ (18)

When AuCN_{ads} is completely reduced, corresponding to $\theta = 0$, Eqs. (8) and (9) apply.

The governing Eq. (3) were solved to determine the concentration profiles of $Au(CN)_2^-$ and HCN, potential at the electrode surface and the surface coverage of $AuCN_{ads}$. The governing equations were linearized around the previous time step using a first-order forward difference method. A three point central difference form is used on governing equations and a second order forward and backward difference form used on boundary conditions. The equations were then solved using from BAND (j) and MATINV subroutines developed by Newman [22]. Convergence on time step size and number of node points was confirmed.

4. Result and discussion

Electrode kinetics—In order to simulate the plating process, the parameters, including diffusion coefficients and electrode-kinetics constants, must be set. The bulk concentrations of simulated species and key experiment conditions are shown in Table 1. We assumed transport parameter from previous studies using a similar electrolyte; these are shown in Table 2. For electrode kinetic parameters, Eqs. (6) and (7) were fit to polarization curves and dc current efficiency measurements. These fits accounted for Au(CN)₂⁻ depletion at the electrode surface. In Fig. 1, the calculated surface concentrations are shown. It is seen that the concentrations of of

Table 1

Experimental conditions that are used for all of the present simulations, unless otherwise noted.

Parameters	Value	
C _{Au,o}	0.04 mol/l	
C _{HCN,o}	0	
i _{avg}	$-20 \mathrm{mA}\mathrm{cm}^{-2}$	
Rotation rate	2500 rpm	



Fig. 1. Concentration of $Au(CN)_2^-$ and HCN as a function of time in response to a step change in current density (indicated in the figure with units of mA cm⁻²), using previously determined current efficiencies [3].

 $Au(CN)_2^-$ and HCN reach a steady state in less than 0.2 s. For the hydrogen evolution reaction, the partial current density is estimated from current efficiency data [3] as a function of applied potential and is used to fit the electrode kinetics.

In Fig. 2, the measured current densities for gold reduction and hydrogen evolution as a function of the ohmic-drop-corrected potentials are presented. The theoretical fit is also shown in Fig. 2. The constants used for electrode kinetics are summarized in Table 3. The calculated Tafel slope of the hydrogen evolution reaction, 0.11 V/dec, is in exact agreement with the value reported by Cheh [10].

On-off pulse plating-In Fig. 3, the concentrations of Au(CN)₂⁻, and HCN at the electrode surface are shown as a function of time; results are given after the concentration profiles have reached

Table 2

Transport properties used in the simulations.

Parameters	Value
Diffusivity of Au(CN) ₂ ⁻ D_{Au} , 10 ⁵ cm ² s ⁻¹ Diffusivity of HCN D_{HCN} , 10 ⁵ cm ² s ⁻¹ Kinematic viscosity v , cm ² s ⁻¹ Specific conductance k , ohm ⁻¹ cm ⁻¹	$\begin{array}{c} 1.67^{a} \\ 2.60^{b} \\ 0.00518^{a} \\ 0.20^{c} \end{array}$

^a From Ref. [5].

^b From Ref. [32].

^c Determined from experiment.



Fig. 2. Experimental polarization curves, with model fit, for the gold reduction and hydrogen evolution reactions.

a quasi-steady response. As the frequency increases, the concentration profiles fluctuate less, approaching the concentration profile established when DC plating at the time-average current density.

The simulated and experimental current efficiencies for on-off pulse plating are shown as a function of peak current density and frequency in Fig. 4. In all cases, the time-average current density $i_{avg} = -20 \text{ mA cm}^{-2}$. This is achieved by adjusting the duty cycle (*i.e.*, the off time) through $i_{avg} = i_{on} \times t_{on}/(t_{on} + t_{off})$.

Good agreement is obtained. It is seen that at low frequencies the current efficiency is lower, close to the current efficiency from DC plating at i_{on} , and at high frequencies the current efficiency is higher, close to the current efficiency from DC plating at i_{avg} . The change of current efficiency with frequency is largely a result of changes of the time–average surface concentration of the Au(CN)₂⁻. At low frequencies, the time–average surface concentration of Au(CN)₂⁻ during the on time, as shown in Fig. 3, is close to that obtained when dc plating at i_{on} . At high frequencies, the time–average concentration is closer to the value obtained when dc plating at i_{avg} .

One of the motivations for constructing a mathematical model is to have the capability to evaluate the effect of process parameters while reducing significantly the number of required experiments. In this study, we focused on the current efficiency, which is an indicator of porosity formation. As an example, the influence of agitation on current efficiency can be predicted, as shown in Fig. 5, which demonstrates the impact of RDE rotation rate on current efficiency. Higher agitation leads to a higher current efficiency by enhancing the mass transfer of gold species to the electrode, leading to a higher near-surface gold concentration. In Fig. 6, the current efficiency as a function of duty cycle, with the same peak current i_{on} and frequency, is shown. As the duty cycle increases, the current efficiency drops. The reason for this change is that a larger time–average plating rate is achieved when the duty cycle is increased, resulting in more surface depletion of Au(CN)₂⁻.

Pulsed reverse plating—In Fig. 7, the simulated $Au(CN)_2^-$ and HCN surface concentrations upon current reversal, along with the EQCM

Table 3	
Electrode kinetics parameters obtained by fitting simulations to data in Fig.	

Reaction	k _i	$\frac{\alpha_{I}}{RT}$
$\begin{array}{l} \operatorname{Au}(\operatorname{CN})_2^- + 2\operatorname{H}^+ + e^- \to \operatorname{Au} + 2\operatorname{HCN} \\ \operatorname{2H}_2\operatorname{O} + 2e^- \to \operatorname{H}_2 + 2\operatorname{OH}^- \end{array}$	$\begin{array}{c} 22.97 mol mA cm^{-2} \\ 0.0002407 mA cm^{-2} \end{array}$	8.7 V ⁻¹ 8.8 V ⁻¹



Fig. 3. Surface concentrations of Au(CN)₂⁻ and HCN as a function of dimensionless time $t/(t_{on} + t_{off})$, after a quasi-steady state is achieved. In all cases $i_{on} = -100 \text{ mA cm}^{-2}$ and $i_{avg} = -20 \text{ mA cm}^{-2}$.



Fig. 4. Current efficiency as a function of frequency. The peak current density is indicated in the figure, and the duty cycle, $t_{on}/(t_{on} + t_{off})$, is adjusted to maintain $i_{avg} = -20 \text{ mA cm}^{-2}$.



Fig. 5. Simulated current efficiency as a function of rotation rate, assuming $i_{on} = -100 \text{ mA cm}^{-2}$ and $i_{avg} = -20 \text{ mA cm}^{-2}$ and $t_{on} = 0.02 \text{ s}$.



Fig. 6. Simulated current efficiency as a function of duty cycle, assuming $i_{on} = -100 \text{ mA cm}^{-2}$, $t_{on} = 0.02 \text{ s}$, and a rotation rate of 2500 rpm. The average current density is given by $i_{avg} = i_{on} \times t_{on}/(t_{on} + t_{off})$.



Fig. 7. Simulated near-surface concentration of $Au(CN)_2^-$ and HCN in response to a step change in current density from i = -5 to +5 mA cm⁻² at zero time. Also shown is the response of the QCM, indicated by the mass change. The dashed line in the figure has a slope of -1.9 mg/C, corresponding to the expected mass change as estimated from Faraday's law, assuming reaction (11).



Fig. 8. Surface concentrations of Au(CN)₂⁻ and HCN as a function of time after a quasi-steady state is achieved in pulsed reverse plating: (a) $i_{rev} = 5 \text{ mA cm}^{-2}$, (b) $i_{rev} = 10 \text{ mA cm}^{-2}$. In both cases, $i_{on} = -100 \text{ mA cm}^{-2}$ and $i_{avg} = -20 \text{ mA cm}^{-2}$, which is achieved by setting $t_{rev} = t_{on} \times (i_{on}/i_{avg} - 1) / (1 + |i_{rev}/i_{avg}|)$.

measurement of electrode mass change, are shown. Immediately after the cathodic current, the electrode mass decreases for the first 0.3 s. The slope of this decrease is-1.9 mg/C, corresponding to a 95% efficiency for the production of soluble gold dissolution products, according to reaction (14). This result is consistent with our assumption that $i_{Au} = i_{rev}$ when $c_{HCN} > 0$. When the mass of the electrode begins to increase, another anodic oxidation reaction commences because HCN is depleted at the electrode.

The areal density of an AuCN_{ads} monolayer, Γ , is calculated to be $\Gamma = 2 \times 10^{-9}$ mol cm⁻² if an atomically smooth monolayer is assumed. The electroplated gold surface can be expected to have significantly greater surface area. To estimate this roughness factor, the QCM data in Fig. 7 were used. It was found that the duration of the monolayer formation, occurring between 0.4 and 0.8 s in Fig. 7, is 0.3 ± 0.1 s when $i_{rev} = 5$ mA cm⁻². This suggests that Γ is in the range of $10-20 \times 10^{-9}$ mol cm⁻², corresponding to a roughness factor between 5 and 10. While a roughness factor of 5–10 may impact the precision of the EQCM, we have not found direct evidence suggesting that this is an important factor for these experiments.

Based on Model 2, the simulated near-surface concentrations of Au(CN)₂⁻ and HCN are shown in Fig. 8, assuming $\Gamma = 10 \times 10^{-9}$ mol cm⁻². From the surface concentration, it is possible to analyze different reaction stages during one pulse cycle. For example, a small plateau in Au(CN)₂⁻ concentration in the beginning of the on time indicates the reduction of adsorbed gold product formed during the reverse time. A large increase of HCN concentration is also seen since this reaction generates HCN. Immediately after the on time, the gold dissolution reaction occurs until the HCN concentration drops to zero. The calculation of surface concentration and duration of each reaction stage may provide insight into the design of the plating waveform.



Fig. 9. The simulated and measured current efficiency as a function of i_{rev} for (a) $t_{on} = 0.2$ and (b) 0.02 s. In both cases, $i_{on} = -100 \text{ mA cm}^{-2}$ and $i_{avg} = -20 \text{ mA cm}^{-2}$. t_{rev} varies according to $t_{rev} = t_{on} \times (i_{on}/i_{avg} - 1) / (1 + |i_{rev}/i_{avg}|)$. Simulation results are given for Models 1 and 2 (for $\Gamma = 10$ and 20 $\times 10^{-9}$ mol cm⁻²).

The use of pulsed reverse plating from a gold–cyanide electrode has not received much attention, in part because the gold dissolution reaction was believed to be insignificant in baths that lack free cyanide [6,29,30]. However, with carefully chosen pulsed reverse waveforms, guided perhaps by simulation, it is possible to achieve plating and partial stripping. This may lead to differing morphologies of the resulting gold deposit [4].

In Fig. 9, the current efficiency data from Models 1 and 2, with Γ values of 10 and 20×10^{-9} mol cm⁻², are compared to experiment. For on-times $t_{on} = 200$ ms, the results from both models agree well experiment for all the anodic currents studied because the formation and reduction of adsorbed gold layer is a small portion of the total coulombs passed per cycle. When $t_{on} = 20$ ms, Model 2 predicts a current efficiency closer to the experimental value. In addition, better agreement is attained when $\Gamma = 20 \times 10^{-9}$ mol cm⁻² for larger anodic current density, 20 mA cm^{-2} . Further improvements to the model are required to achieve better agreement

with experiment. For example, the reduction of adsorbed gold is assumed to occur at 100% efficiency, and the anodic reactions are assumed to occur in stages, with soluble gold dissolution, followed by formation of an oxidized layer, followed by oxygen evolution. Clearly, the modeling approach is simplified, and we feel novel experiments are required to develop a more refined model without excessive *a priori* unknown parameters.

5. Conclusions

Numerical simulations of gold plating accurately capture the current efficiencies obtained by on-off plating of cobalt hard gold. However, the prediction of current efficiencies obtained during pulse-reverse plating is more difficult. Consistent with QCM data, simulations assume that, during oxidation, soluble gold-oxidation products are prevalent until the near-electrode, excess cyanide, generated by the gold reduction reaction, is depleted. At low frequencies, good agreement with experiment is seen, while at higher frequencies agreement is only fair. High frequency data are more difficult to simulate because the formation of oxidized gold surface layers account for a more significant fraction of the coulombic charge per cycle, and we believe the treatment of these layers requires the most model refinement.

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