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Thin Layer Electrochemical Studies Using Controlled Potential or Controlled Current

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► A new, versatile electrode design suitable for thin layer electrochemical studies was developed, and its accuracy and practicality were verified. The use of both platinum-metal and mercury-coated platinum as working electrode materials is discussed. Errors resulting from residual currents were investigated. Rapid thin layer chronopotentiometric studies of the ferri-ferrocyanide couple at a polished platinum electrode gave results in good agreement with theory. Diffusion coefficients were determined using the chronopotentiometric technique. The basic equations describing chronoamperometry in the thin layer are presented and experimentally verified using the Cu(II)-Cu(0) and the ferri-ferrocyanide couples.

THEORY and technique of studying small solution thicknesses chronopotentiometrically were introduced by Christensen and Anson (2). These authors later applied the technique to the study of kinetics of hydrolysis of *p*-benzoquinoneimine (3). Hubbard and Anson (5) published thin layer electrode designs which were more versatile than those employed previously. Osteryoung and Anson (8) used thin layer chronopotentiometry to show that adsorbed iodide ion was not oxidizable at the same potential as the solution species.

This work presents an improved thin layer electrode design. The design allows the use of a variety of electrode materials as working electrodes, including the smooth platinum and mercury-coated platinum surfaces investigated here. Solution

thicknesses from 1×10^{-3} cm. to 1 cm. are readily obtained. The problem of *iR* drop between the working and the reference electrodes is reduced significantly, and the problem of contamination of the solution by oxygen is overcome. The same basic assembly can be used to study a thin layer of solution bounded by one working electrode and an inert barrier; two equipotential working electrodes; or two working electrodes with independent potential and/or current control (Figure 1).

EXPERIMENTAL

The basic thin layer electrode assembly was constructed from a 0- to 2-inch micrometer with attachment (L. S. Starrett Co., Athol, Mass.). A precision thimble (Starrett No. T2211) allowed direct reading to one ten-thousandth of an inch. To modify the micrometer for use as an electrode, the spring loading in the precision thimble was replaced by a friction washer. A platinum disk was silver-soldered onto the face of the micrometer spindle and the platinum tip machined flat and lapped to a mirror finish. The area of the electrode face, calculated from the outside diameter of the micrometer spindle, was 0.278 sq. cm. The Teflon collar (Figure 2 b) was pressed onto the micrometer spindle, resulting in a solution-tight seal between the metal and the Teflon. The collar was positioned so that the platinum tip extended approximately 0.001 inch past the face of the collar (Figure 2).

A cup machined from Teflon, designed to hold the sample solution, was mounted on a detachable anvil (Starrett 212). An optically flat glass disk was press-fitted into the bottom of the Teflon cup and rested flat against the face of the detachable anvil (Figure 2 d).

A circular piece of platinum gauze, placed around the inside of the cup and attached to a platinum wire lead, constituted the auxiliary electrode.

A Lucite cover was placed over the cup to maintain a nitrogen atmosphere over the solution. The cover, constructed in two sections for easy placement and removal, was provided with holes to allow insertion of the arm of an S.C.E., the delivery tube of the deaeration bottle, and a stream of nitrogen (Figure 3).

The solution was deaerated prior to introduction into the Teflon cup. The deaeration bottle was fitted with a gas dispersion tube, a delivery tube, and a small vent. When the vent was covered by the thumb, the increased nitrogen pressure forced the solution to flow out of the delivery tube. The first few milliliters of solution were discarded to assure freedom from oxygen contamination.

Mercury-Coated Platinum Electrode. For the mercury-coated platinum electrode assembly, a Starrett T2F1 0- to 2-inch micrometer was employed. A platinum tip and Teflon collar were fixed to the spindle of the micrometer in the same manner as described for the platinum thin layer electrode. The platinum was coated with mercury by successively polishing with rouge and dipping into mercury, a technique similar to that used by Moros (7). A flat spatula, covered with a piece of filter paper impregnated with a fine grade of lens rouge, was used for polishing.

After thorough amalgamation, the tip was washed with a stream of mercury from a polyethylene wash bottle. Thorough coating of the surface was essential to obtaining reproducible runs. Excess mercury was removed by suction through a fine capillary connected to an aspirator. The mercury-coated surface could be used repeatedly unless the potential of the electrode was allowed to become sufficiently negative for appreciable hydrogen evolution or sufficiently positive for oxidation of the mercury surface.

Normally, the electrode surface was washed with mercury and the excess removed with the capillary before each run. The mercury-coated platinum

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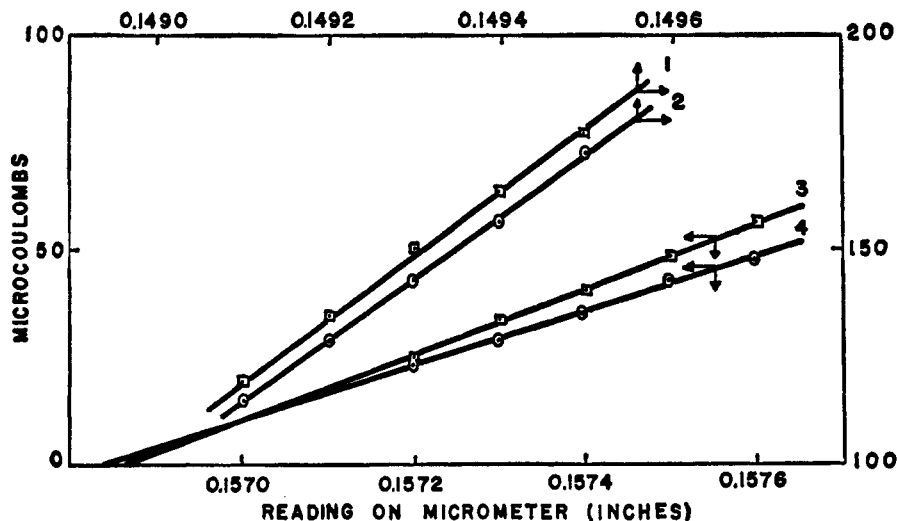


Figure 4. Calibration curves

mM $\text{Cu}(\text{NO}_3)_2$ in 1.0M KNO_3 , Hg-coated Pt electrode

1. Chronopotentiometric data, $i = 5 \mu\text{A}$, intercept 0.14829 cm.
2. Chronoamperometric data, potential stepped from + 0.15 to -0.20 volt; intercept, 0.14831 cm.

mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.5M Na_2SO_4 , Pt electrode

3. Chronoamperometric data, potential stepped from -0.15 to -0.30 volt; intercept 0.15688 cm.
4. Chronopotentiometric data, $i = 2.5 \mu\text{A}$, intercept 0.15683 cm.

electrode was placed in a nitrogen atmosphere as soon as possible after preparation to minimize oxidation of the surface by oxygen. When not in use, the electrode surface was covered with a nitrogen-filled balloon.

An S.C.E. was used as the reference electrode for both the controlled-current and controlled-potential studies. Philbrick UPA-2 and chopper-stabilized K2-W operational amplifiers, powered by a Philbrick R-300 power supply, with appropriate circuitry, were used to obtain the desired instrumentation. The input and feedback circuits are shown in Figure 1. A Sargent Model SR recorder was used for recording the integrated current-time curves and the potential-time curves for times longer than about 5 seconds. For the faster potential-time curves, a Sanborn Model 151-100A single channel recorder with a Model 150-400 drive amplifier and power supply and a Model 15-1800 stabilized d.c. pre-amplifier were used.

All solutions were prepared from

J. T. Baker reagent grade chemicals. The $1.0 \times 10^{-3}\text{M}$ potassium ferricyanide was 0.5M in sodium sulfate supporting electrolyte. The $1.040 \times 10^{-3}\text{M}$ cupric nitrate solution was 1.0M in potassium nitrate supporting electrolyte.

After deaeration of the solution, the cup was filled from the deaeration bottle. The desired solution thickness was established by turning the thimble of the micrometer to the appropriate setting, based on a previous calibration. Electrical contact with the working electrode surface was made by attaching a lead to the body of the micrometer.

DISCUSSION

An important aspect of using thin-layer electrodes is accurate knowledge of the effective thickness of the solution (2). With the micrometer electrode different solution thicknesses are readily obtained. However, it is necessary

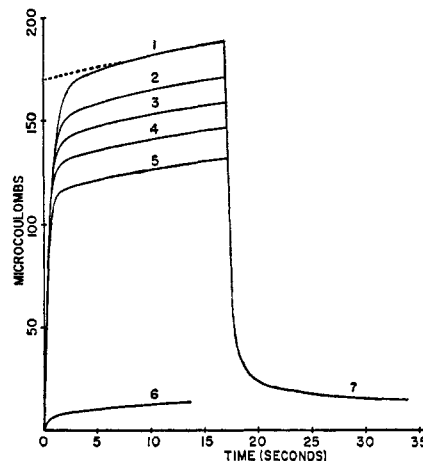


Figure 5. $Q-t$ curves at an Hg-coated Pt electrode

mM Cu^{+2} in 1M NO_3^- , potential stepped from +0.15 to -0.20 volt and vice versa. Solution thickness: 1. 3.05×10^{-3} ; 2. 2.80×10^{-3} ; 3. 2.54×10^{-3} ; 4. 2.28×10^{-3} ; 5. 2.03×10^{-3} cm.; 6. background curve on 1M KNO_3 ; 7. stripping curve

first to establish the micrometer setting at which the solution thickness is zero. One method of finding the effective solution thickness is the following: using chronopotentiometry, a plot of $i\tau$ as a function of micrometer setting will yield an intercept at $i\tau$ equal to zero, which will represent a solution thickness of zero (2).

$$l = i\tau/nFAC^\circ$$

For chronoamperometry, the analogous plot of Q , the coulombs of electricity passed, as a function of micrometer setting yields the zero-thickness setting at $Q = 0$. Once this is done for a given electrode, one may accurately and directly set any desired solution thickness from less than 1.0×10^{-3} cm. up to the depth of the solution in the cup. The screw of the micrometer is precisely machined so the reproducibility of the settings is usually limited by the precision with which the worker can read the scale. The calibration curves for the platinum thin-layer electrode are shown in Figure 4.

The intercepts were calculated by the least-squares method. The intercept based on the data from controlled potential electrolysis with integrated current was a micrometer reading of 0.15688, and the intercept based on controlled current data was at a reading of 0.15683, a difference of 0.00005 inch. This difference is small and consistent. The reproducibility of data at a given micrometer setting, using a given technique—e.g., controlled potential or controlled current—was $\pm 2 \times 10^{-5}$ inch (it should be noted that the slopes of the two lines are different).

Figure 4 also shows the calibration curve for the mercury-coated platinum

Table I. Reproducibility of Electrochemical Studies Using Mercury-Coated Electrode

Data taken on $1.040 \times 10^{-3}\text{M}$ Cu^{+2} in 1.0M KNO_3
Electrode area = 0.278 sq. cm.
Each average represents six different mercury coatings

Soln. thickness based on calibration curve of Figure 4, cm. $\times 10^{-3}$	Av. chronopot. transition time at 5 μA , sec.	Av. $i\tau$ $\mu\text{coulombs}$	Rel. std. dev., %	Av. integrated current from chronoamp., $\mu\text{coulombs}$	Rel. std. dev., %
2.03	23.8	119	± 1.6	115	± 1.7
2.28	27.0	135	± 3.1	129	± 2.0
2.54	30.0	150	± 2.3	143	± 2.3
2.80	32.8	164	± 1.4	157	± 1.6
3.05	35.6	178	± 1.3	173	± 1.9

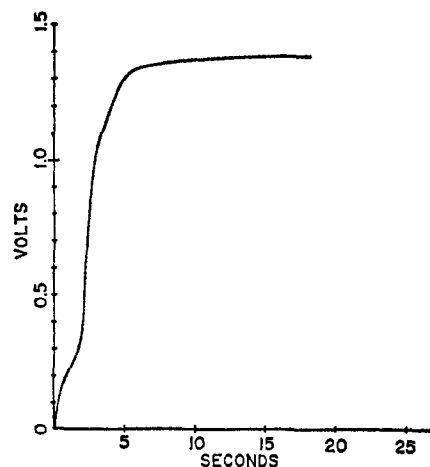


Figure 6. Chronopotentiogram of 1.0 M KNO₃ with the mercury-coated thin layer electrode

$l = 2.28 \times 10^{-3}$ cm.; current = 5 μ a.; electrode area = 0.278 sq. cm.

electrode, based on the data in Table I. Setting this electrode involves re-producing the mercury coating on the platinum face. Several runs representing renewal of the mercury surface by the procedure already given are summarized in Table I. A representative set of integrated current-time curves is shown in Figure 5.

The useful negative potential range is much greater with the mercury-coated platinum than with the polished platinum surface. Hydrogen evolution does not occur until approximately -1.3 volts vs. S.C.E., as may be seen from Figure 6. In the study of adsorption and electrochemical processes, irreversible on platinum, by the thin-layer technique, the unique properties of mercury as an electrode material can be utilized.

An important portion of the residual current in thin layer electrolysis is caused by the edge effect—diffusion of the electroactive species into the thin layer from the perimeter of the volume element. This cylindrical edge is exposed to semi-infinite diffusion from the bulk of the solution, causing a residual current proportional to the concentration of all species electrolyzed at the potential of the working electrode. Complete elimination of this edge effect poses a difficult design problem because a solution contact must be made with the reference and auxiliary electrodes.

Contributions to the current from reduction of surface metal oxides or catalytic reduction of the solvent will be more important in thin layer than in semi-infinite techniques. A typical thin layer of solution ($l = 2 \times 10^{-3}$ cm., $A = 0.3$ sq. cm., $C^\circ = 10^{-3}M$) contains only 6×10^{-10} mole of electroactive species, equivalent to approximately three monolayers on the electrode surface.

In practice, residual currents less than 1 μ a. per sq. cm. have been attained by excluding oxygen, using small solution thicknesses, and minimizing the current contribution from electrolysis of hydrogen ion or formation or reduction of surface metal oxides.

To verify that residual current is in part caused by an edge effect, the Teflon collar was slipped slightly past the electrode face. The micrometer screw was turned to a setting which previously corresponded to a thickness of 2.03×10^{-3} cm. However, at this setting the Teflon collar touched the bottom of the cup, causing an upward force on the spindle of the micrometer. Recalibration showed that this caused the thickness to be 2.75×10^{-3} cm., as a result of backlash in the micrometer screw. The residual current was reduced by about one half, but the iR drop between the reference and working electrodes was increased, causing a shift in the measured reduction potential of Cu²⁺ by about -0.06 volt.

The error caused by residual current depends on the time required for the electrochemical measurement, and controlled current experiments can be carried out at shorter times than those indicated by Hubbard and Anson (5).

A practical lower limit to the length of transition times was not encountered using the electrode design shown in Figure 3. The ill-defined chronopotentiograms with transition times less than 10 seconds reported by Hubbard and Anson (5) might have been caused by the proximity of the working electrode to the auxiliary electrode; this results in poor current distribution over and large resistance drop across the electrode face. The large current required for reduction of the concentrated solutions used made the resistance factor more important. In the present work, transition times as short as 0.2 second were obtained without difficulty, as may be seen from the chronopotentiogram shown in Figure 7.

Shown in Figure 8 is a plot of the transition time vs. $1/i$ for different solution thicknesses. The linearity of

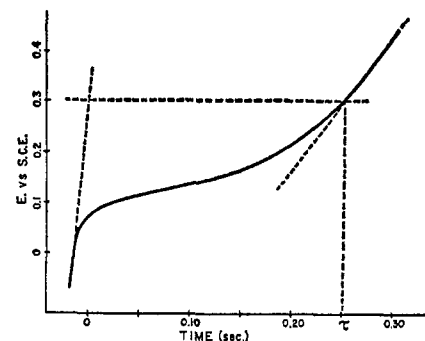


Figure 7. Short-time thin layer chronopotentiogram

Platinum thin-layer electrode; $1.0 \times 10^{-3}M$ K₃Fe(CN)₆ in 0.5M Na₂SO₄; $l = 1.12 \times 10^{-3}$ cm.; current = 100 μ a.; electrode area = 0.278 sq. cm.; $\tau = 0.25$ sec.

these plots indicates good agreement with the theoretical relationship:

$$\tau = \frac{nFAC^\circ}{i} - \frac{l^2}{3D} \quad (1)$$

The transition times were measured graphically by the "method of Kuwana" (9). Equation 1 should hold for times down to about 0.2 second because the exponential term of Equation 2

$$\frac{nFAC^\circ}{i} - \frac{l^2}{3D} = \tau - \frac{2l^2}{\pi^2 D} \sum_{k=1}^{\infty} \frac{1}{k^2} \exp\left(-\frac{Dk^2\pi^2\tau}{l^2}\right) \quad (2)$$

is negligible at these times.

Diffusion Coefficients. Because a plot of τ vs. $1/i$ has an intercept with the τ axis at $-l^2/3D$ and because l is determined on the basis of the calibration plot of Figure 4, diffusion coefficients can be determined without a knowledge of the solution concentration or the electrode area. The $l^2/3D$ intercepts of the plots shown in Figure 8 give the values shown in Table III. The data for Figure 8 and the values given in Table III are based on Table II. The average value of 0.45×10^{-5} sq. cm./second found is about one half that

Table II. Chronopotentiometric Data Taken at Current Densities Such That $l^2/3D$ Term Is Significant

1.0 $\times 10^{-3}M$ Fe(CN) ₆ ³⁻ in 1.0M Na ₂ SO ₄ ; electrode area = 0.278 sq. cm.					
1/ <i>i</i> , μ a. ⁻¹	Solution thickness, cm. $\times 10^{-3}$				
	0.864	1.12	1.37	1.62	1.88
Transition time, sec.					
0.01	0.20	0.25	0.26	0.25	0.27
0.02	0.45	0.52	0.54	0.66	0.77
0.03	0.70	0.82	0.98	1.10	1.29
0.05	1.18	1.46	1.71	1.96	2.30
0.07	1.72	2.08	2.43	2.86	3.27
0.08	1.96	2.36	2.89	3.38	3.73
0.10	2.40	3.04	3.56	4.23	4.85
0.11	2.72	3.31	3.89	4.72	5.40
Exptl. slope	2.50	3.09	3.70	4.48	5.09
Theoret. slope	2.32	3.00	3.67	4.36	5.04

Table III. Diffusion Coefficient Values Based on $l^2/3D$ Intercepts of Plots in Figure 8

Least-squares method used to calculate intercepts from data given in Table II

Cm. $\times 10^{-3}$	$\frac{l^2}{3D}$ (sec.)	D , sq. cm./sec. $\times 10^5$
0.864	0.0502	0.49
1.12	0.0883	0.47
1.37	0.140	0.45
1.62	0.236	0.37
1.88	0.252	0.47
		Av. 0.45

given by Kolthoff and Lingane (6). Application of the thin layer electrochemical method to the study of diffusion coefficients is being further investigated.

Thin Layer Chronoamperometry. Consider an electroactive solution species within the finite boundaries at zero and l , such that $0 < x < l$. Also, consider the electrode surface to be at l . With the initial condition $C(x,0) = C^\circ$ and the boundary conditions $\partial C(x,t)/\partial x|_{x=0} = 0$ and $C(l,t) = 0$ for chronoamperometry, one may readily derive an expression for $C(x,t)$ by Laplace transforms or by reflection and superposition (4). The expression, previously derived for similar problems in heat conduction, converges most rapidly for small times and is given by (1).

$$C(x,t) = C^\circ - C^\circ \sum_{n=0}^{\infty} (-1)^n \times \left[\operatorname{erfc} \frac{(2n+1)l-x}{2\sqrt{Dt}} + \operatorname{erfc} \frac{(2n+1)l+x}{2\sqrt{Dt}} \right] \quad (3)$$

Another form of this equation, which converges more rapidly for solutions at long times, is given by:

$$C(x,t) = \frac{4C^\circ}{\pi} \times \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \left[\exp \left(-\frac{D(2n+1)^2\pi^2 t}{4l^2} \right) \right] \left[\cos \frac{(2n+1)\pi x}{2l} \right] \quad (4)$$

Equation 3, valid for short times, becomes more unwieldy at longer times and is not a valid solution of the differential equation at the limit as t approaches infinity. Similarly, Equation 4 is not a valid series solution as t approaches zero. This is also true of the chronopotentiometric equations presented by Christensen and Anson (2). Equation 1 of those authors is the series valid at long times, and Equation 2 is valid for short times.

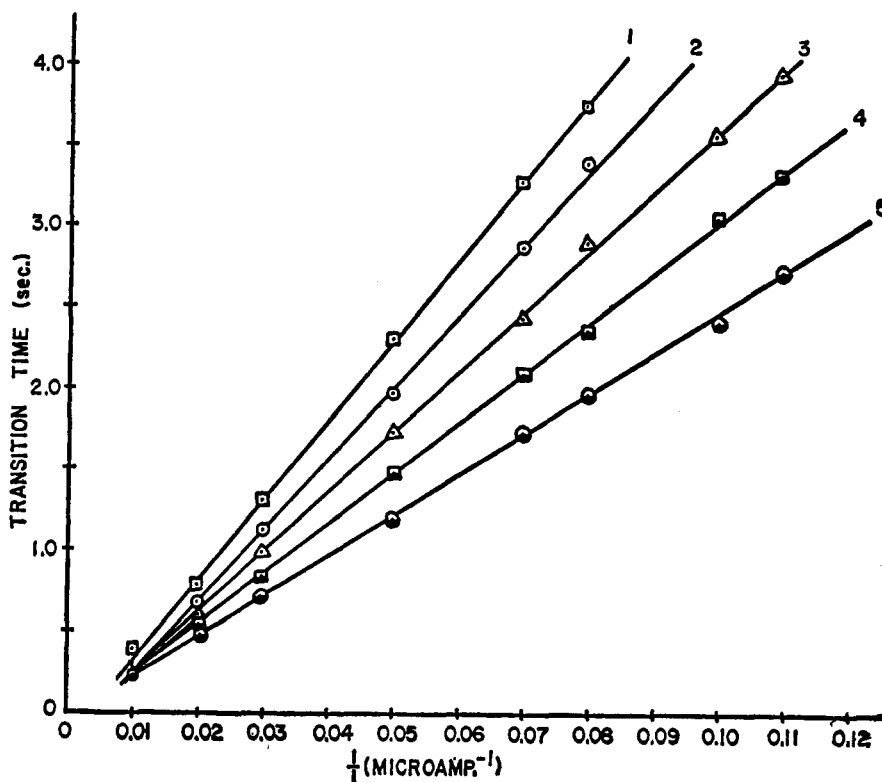


Figure 8. Dependence of τ on $1/i$ at different solution thicknesses

Pt electrode area, 0.278 sq. cm.; mM $K_3Fe(CN)_6$ in 0.5M Na_2SO_4 . Solution thickness: 1. 1.88×10^{-3} ; 2. 1.62×10^{-3} ; 3. 1.37×10^{-3} ; 4. 1.12×10^{-3} ; 5. 0.864×10^{-3} cm. Although only data to $\tau \cong 4$ sec. are shown, the data included transition times from about 0.25 sec. to about 20 sec. with the same linearity shown here

The expression for current at the electrode surface as a function of time may readily be obtained by multiplying $\partial C(x,t)/\partial x$ by $nFAD$ and substituting $l = x$.

$$i_{(l,t)} = \frac{nFAD^{1/2}C^\circ}{\pi^{1/2}t^{1/2}} \times \sum_{k=0}^{\infty} (-1)^k \left[\exp \left(-\frac{k^2 l^2}{Dt} \right) - \exp \left(-\frac{(k+1)^2 l^2}{Dt} \right) \right] \quad (5)$$

This equation shows that when $l^2 < Dt$, the current decays rapidly. The use of controlled potential with integrated current allows not only precise control of the potential throughout the experiment but also rapid depletion of the species being studied. A partial correction for residual current and charging of the double layer may be made from an integrated current-time curve on the supporting electrolyte at the same potential used for the electrolysis. Point by point subtraction of this background curve from the i - t curve, obtained from a run with the depolarizer present, yields a measure of the amount of depolarizer present.

Many of the advantages of the thin-layer electrochemical cell have already been pointed out (2, 3, 5, 8). One is

that, in the times required for many analytical processes, one has homogeneous diffusional mixing of the solution in the volume element being studied. Further studies are underway for applying this principle to the coulometric analysis of ion mixtures by controlled potential with integrated current.

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