



Rapid reduction of U(VI) on activated platinum wire gauze electrode for the primary coulometric determination of uranium

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Abstract

A large enhancement in the active area of a hollow cylindrical platinum wire gauze electrode was achieved by repetitive multilayer growth of oxide followed by its reduction. Growth of oxide was obtained by a combination of chemical and electrochemical treatments. Enhancement in the active area of the electrode was checked by determining the time taken for the quantitative reduction of U(VI) to U(IV) at a controlled potential of -0.150 V vs SCE in 1 M H_2SO_4 . A six-fold decrease in the reduction time was observed, indicating a corresponding six-fold increase in the active area of the electrode. The enhanced activity of the electrode was found to decay on ageing. Determination of uranium was carried out by a successive addition technique using the activated platinum wire gauze electrode and carrying out the reduction U(VI) to U(IV) at a controlled potential of -0.150 V vs SCE. Precision and accuracy of better than $\pm 0.2\%$ were obtained at 5 to 10 mg levels of uranium. This demonstrates the applicability of a platinum electrode, instead of the conventionally used Hg electrode, for determination of uranium by primary coulometry.

1. Introduction

Coulometry is an absolute technique since it is based on fundamental physical quantities. This obviates the need to carry out analysis of a standard reference material along with the unknown samples and avoids the use of chemicals for reduction or oxidation. It is capable of giving high precision and accuracy at milligram levels. It provides the possibility of remote handling of radioactive samples in nuclear laboratories. Owing to these advantages, coulometry is generally employed for the determination of uranium. The only primary requirement for the determination is that the potential of the electrode should be controlled to a value at which a single reaction occurs quantitatively with 100% current efficiency.

Determination of uranium on a platinum electrode is not a straightforward matter, since difficulties arise due to HER at the potential (-0.350 V vs SCE) needed for the reduction of U(VI). Therefore it is routinely carried out by primary coulometry in 1 M H_2SO_4 at a Hg pool electrode at a potential of -0.350 V vs SCE [1–4].

Due to hazards associated with the use of mercury, solid electrodes are now preferred. There are methods for the determination of uranium using solid electrodes like silver [5], graphite [6], platinum [7–9] and gold [10]. Silver dissolves in sulfuric acid electrolyte, and the blank

values are too large and irreproducible on graphite electrode. HER on platinum can be suppressed by dissolving trace amounts of Bi(III) or Pb(II) in appropriate electrolyte and secondary reactions are involved. The time taken for quantitative reduction of U(VI) on gold was found to be too long for routine analyses.

In coulometry, the speed of electrolysis determines the time taken for quantitative reduction or oxidation of analyte, and depends on the optimum potential, rate of stirring, temperature, working electrode active surface area (A), and the solution volume (V) in the cell. The larger the AV^{-1} ratio, the higher is the current and shorter is the time for quantitative electrolysis [11, 12].

In electrochemistry, platinum is often chosen as the electrode for fundamental and technological applications due its excellent catalytic activity and marked resistance to corrosion. The possibility of enhancing the catalytic activity of platinum was first demonstrated by Burke et al. [13]. It was reported that on prolonged anodization of platinum in 1 M H_2SO_4 , changes in the nature of the oxide film occur [14–16]. These films were characterized as a multilayer phase oxide that, on reduction, produce a change in surface morphology to a sponge like porous surface film [17–26]. This porous electrode shows enhanced catalytic activity, since its real active surface area is greater than its geometrical surface area. This effect has been confirmed by others [27–37].

However, the porous structure, and hence the enhanced catalytic activity of the electrode, is temporary, since the electrode regains its original compact structure on ageing [22, 36].

This paper presents observations made on the enhancement of the active surface area of a large cylindrical hollow platinum wire gauze by combination of chemical and electrochemical oxidation followed by electrochemical reduction, and its application for the determination of uranium by primary coulometry.

Since the motivation of these studies was to activate the platinum wire gauze for application to analytical purposes, the physical nature of the oxides formed on it was not studied. However, the enhanced catalytic activity was conjectured by observing a decrease in the time taken for quantitative reduction of U(VI).

2. Experimental details

2.1. Reagents

All reagents used were of AR/GR grade. Water distilled from a quartz apparatus was used for preparing the reagents. High purity argon gas was purged continuously over the surface of the contents of the cell during experiments.

2.2. Electrochemical instrumentation

A EG&G (PARC model 300) coulometric system was used. The working electrode was hollow cylindrical platinum wire gauze of 0.025 m height and 0.035 m diameter. The auxiliary electrode was a thin platinum wire. The reported potentials were with respect to the saturated calomel electrode (SCE). All the experiments were carried out at ambient temperature.

2.3. Preliminary experiments

In view of our objective to exploit the reported unusual high catalytic activity exhibited by platinum after growth of thick multilayer phase oxides, preliminary experiments were carried out to select a suitable potential for quantitative reduction of U(VI) on a normal platinum electrode with 100% current efficiency in 1 M H₂SO₄ electrolyte.

25 mL of 1 M H₂SO₄, which was just sufficient to submerge the platinum wire gauze electrode, was taken in the electrolysis cell and electrolysed at a controlled potential to find the potential for HER. Similarly, the decomposition potential of U(VI) was also determined.

A weighed aliquot of a standardized uranium solution in 1 M H₂SO₄ was taken directly in 25 mL of 1 M H₂SO₄ electrolyte. Preelectrolysis followed by reduction of U(VI) was carried out at controlled potentials of +0.085 V and -0.150 V, respectively, to determine the time taken for quantitative reduction of U(VI) to U(IV).

2.4. Activation of the platinum wire gauze electrode

The primary requirement for enhancing the active area of platinum is to grow multilayer oxide films. Typically, this can be achieved by applying a large number of potential anodization–cathodization (A–C) cycles in 1 M H₂SO₄ between high positive (>1.2 V) and less positive (<1.0 V) potentials. The recommended potential a.c. cycles range from 10 000 to 25 000 cycles [32] or more than two days continuously [21]. Since the instrument employed was operable only manually, the recommended potential A–C cycling was found to be impractical.

In the present work, initial strain in the platinum electrode was produced by chemical oxidation followed by electrochemical reduction. When the electrode showed some enhancement in the active area, potential cycling technique was employed for further enhancement of the active area of the platinum electrode.

2.4.1. Chemical treatment

The electrode was immersed in a freshly prepared hot mixture of a saturated solution of K₂Cr₂O₇ in concentrated H₂SO₄ for about 10 min. The electrode was washed with distilled water and reduced electrochemically in 1 M H₂SO₄ at a potential of -0.150 V until the current reached about 25 μA. The time taken for quantitative reduction of U(VI) to U(IV) at a potential of -0.150 V in the same electrolyte was noted. The cycles of chemical oxidation followed by electrochemical reduction were repeated successively until the time taken for quantitative reduction of uranium decreased. Later, the oxidation was carried out by potentiostatic, and also by galvanostatic modes in 1 M H₂SO₄.

2.4.2. Electrochemical activation

(a) *Potentiostatic A–C cycling.* Since platinum is oxidized at a potential more positive than 1.2 V, studies of the effect of the anodization potential on the formation of surface oxides were carried out at potentials more positive than 1.2 V. The electrode was submerged in 1 M H₂SO₄ and was anodized at different controlled preselected potentials for 15 min. This was immediately followed by cathodization in the same electrolyte at -0.150 V vs SCE until the current reached the background level of 25 μA. The A–C cycles were repeated in the same electrolyte. The potentials employed for anodization of the platinum electrode were +1.4, +1.5 and +1.6 V in independent experiments.

(b) *Galvanostatic anodization–potentiostatic cathodization.* The electrode was anodized in 1 M H₂SO₄ at different preselected currents for different durations followed by reduction at -0.150 V vs SCE in the same electrolyte until the current reached 25 μA. The different currents employed for anodization of the platinum electrode were 1, 2 and 3 mA in independent experiments.

2.4.3. Enhancement in the active area

After each activation experiment, the electrode was checked for any enhancement in the active area. An aliquot of uranium solution was added directly to the same electrolyte used for activation of the electrode and electrolysed at -0.150 V. The time taken for the current for the reduction of U(VI) to reach to background level was taken as a measure of the electrode activation.

The electrode was allowed to age after each experiment so that it regained its preactivated normal surface prior to performing a further experiment.

2.5. Primary coulometric determination of uranium

The electrolyte (25 mL of 1 M H_2SO_4) was conditioned by cycling between $+0.085$ V and -0.150 V to obtain a constant blank. A weighed aliquot of uranium solution was added to this preconditioned electrolyte. Preelectrolysis and reduction of U(VI) were carried out at potentials of $+0.085$ V and -0.150 V, respectively. Electrolysis was terminated at the background current level. The coulometer reading corresponding to U(VI) reduction was noted. Determination of uranium in different aliquots was continued by successive addition of uranium aliquots in the same electrolyte. The coulometer reading was reset prior to carrying out the next experiment.

3. Results and discussion

3.1. Preliminary experiments

Current–potential curves for HER and also for the reduction of U(VI) to U(IV) in 1 M H_2SO_4 are shown in Figure 1. HER begins at potentials more negative than

-0.18 V. Therefore, it may be concluded that U(VI) may be reduced in 1 M H_2SO_4 on a platinum electrode at potentials less negative than -0.18 V vs SCE with 100% current efficiency. A potential of -0.150 V was, therefore, chosen for the studies for reduction of U(VI). It was observed that the reduction was not only quantitative but also 100% current efficient. However, the time taken was in the range of 100 to 120 min.

3.2. Activation studies

3.2.1. Chemical treatment

After about 25 successive hybrid chemical and electrochemical pretreatments, some enhancement in the activity of the electrode was observed. Further enhancement in the activity was carried out by electrochemical A–C cycles in 1 M H_2SO_4 .

3.2.2. Electrochemical activation

(a) *Potentiostatic A–C cycling.* The results of the studies of potentiostatic A–C cycles are shown in Figures 2–4. The quantity of reduction charge in the last A–C cycle of the respective number of A–C cycles is shown in Figure 2. The reduction charge associated with the first A–C cycle was large when compared to the next successive A–C cycles, particularly at $+1.4$ V and $+1.5$ V. This higher reduction charge was due to the fact that the surface of the electrode was cleaned in freshly prepared hot chromic acid and was washed with distilled water and then anodized. Hence the observed charge is due to the effect of both chemical and electrochemical anodic oxidation, whereas the reduction charge in the successive A–C cycles was due only to potentiostatic anodization. Further, the reduction charge was found to reach a limit after a certain number of A–C cycles, seven, five and three A–C cycles for the

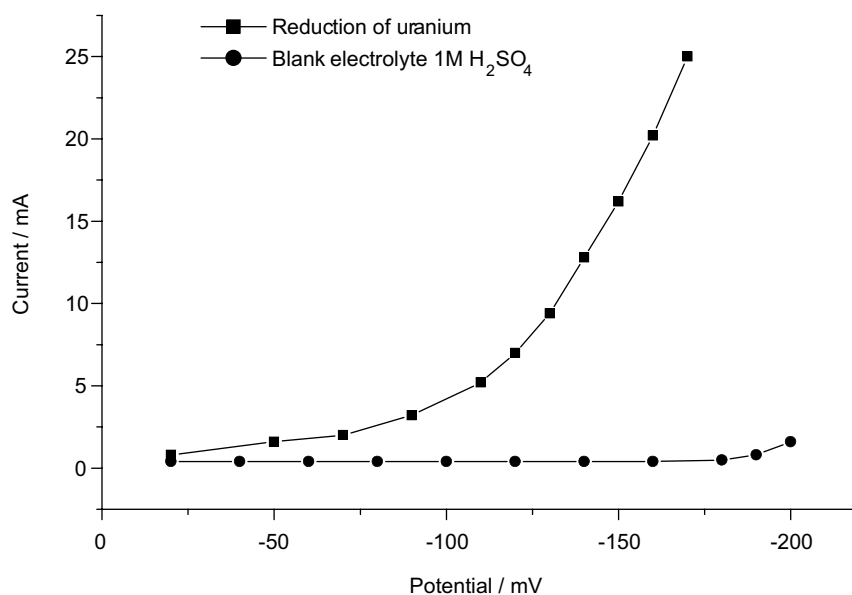


Fig. 1. Current–potential curves for 1 M H_2SO_4 , and for reduction of U(VI) in 1 M H_2SO_4 on electrolytically cleaned platinum wire gauze electrode. Potential of electrode was increased in steps and the corresponding peak currents were plotted.

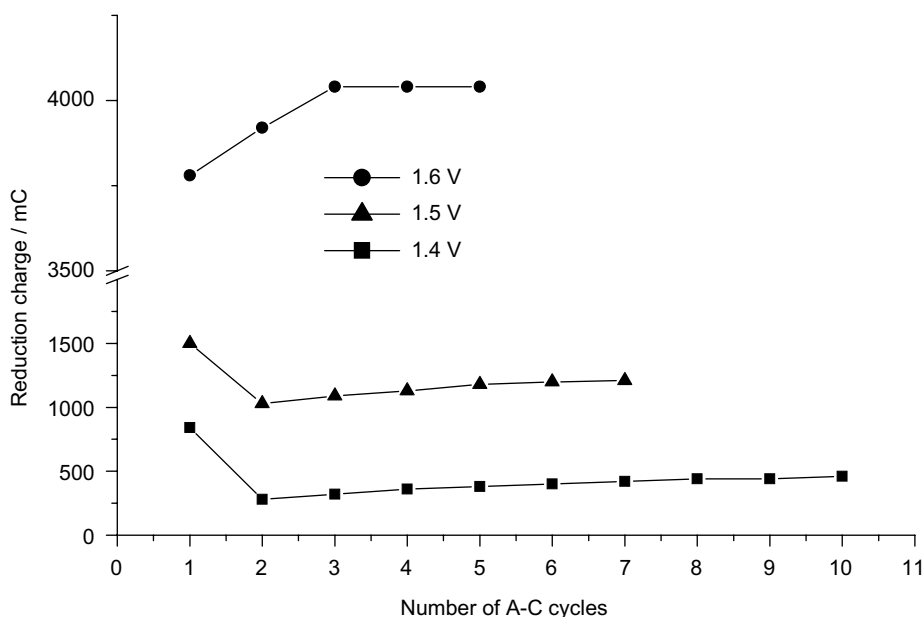


Fig. 2. Quantity of reduction charge in the last cathodization cycle of the respective number of potentiostatic A–C cycles. The platinum wire gauze electrode was anodized in 1 M H₂SO₄ at controlled preselected potential for a period of 15 min and cathodized at a controlled of –0.150 V vs SCE to the background current of 25 μ A. Potentiostatic A–C cycles were performed successively in same electrolyte.

potentiostatic anodization potential of +1.4, +1.5 and +1.6 V, respectively.

The variation in the amount of reduction charge in the last A–C cycle of the respective number of potentiostatic A–C cycles is shown in Figure 3. It is clear that the quantity of reduction charge is in multiple proportions for a given number of A–C cycles. This may be attributed to the formation of higher valence oxides at higher anodization potentials.

The variation in the duration of reduction of charge after completion of the respective number of different potentiostatic A–C cycles is shown in Figure 4. The duration is proportional to the amount of reduction charge for a given number of A–C cycles at different anodization potentials. The difference in the duration of reduction of charge suggests that different steps are involved in the reduction.

The relation between the quantity of oxide and the time taken for its reduction, and also for U(VI) are

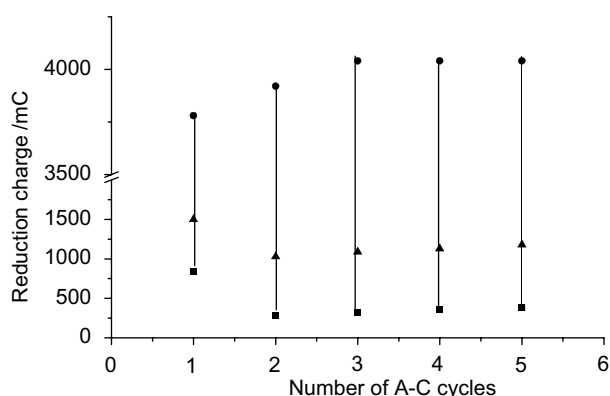


Fig. 3. Legend is same as in Figure 2.

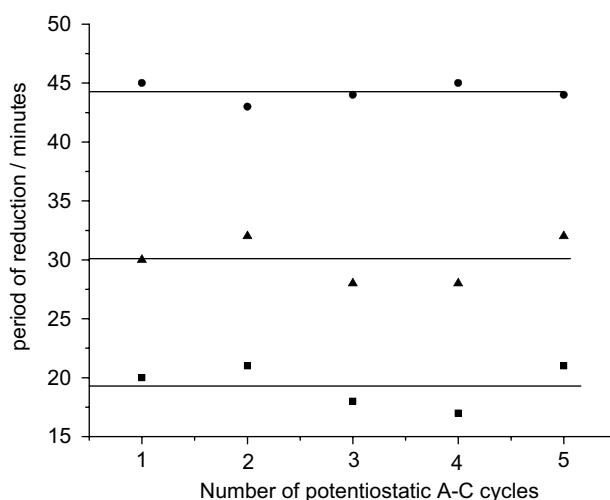


Fig. 4. Period of reduction of oxide in the last cathodization cycle of the respective number of potentiostatic A–C cycles. Experimental conditions same as in Figure 2.

shown in Figure 5. It is seen that the period of reduction of oxides is independent of the quantity of oxide at a particular anodization potential, but increases with increasing anodization potential, that is, 20, 30 and 45 min for anodization at +1.4, +1.5 and +1.6 V, respectively. However, the period of reduction of uranium decreases and reaches a plateau. The plateau indicates the limit to the enhancement of the electrode active surface area. The plateau value, 20 min, is the same at all anodization potentials. This supports the view that, at higher anodization potentials, higher valence oxides are formed and also that a surface having the same active area is produced on reduction of the oxides, since the period of reduction of an analyte in

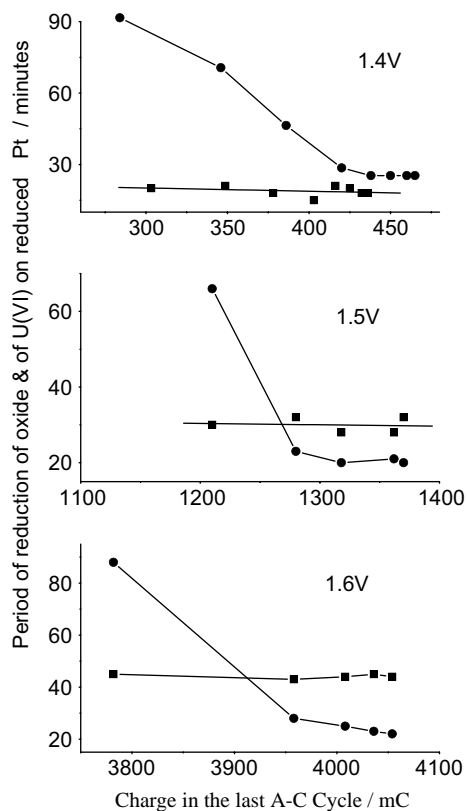


Fig. 5. Period of reduction of oxide in the last cycle of the respective number of A-C cycles and of U(VI) on the reduced platinum electrode. After each cathodization cycle an aliquot of uranium was added in the same electrolyte and reduced at -0.150 V vs SCE to the background current of $25 \mu\text{A}$. Key: (■) reduction of oxide, (●) reduction of U(VI).

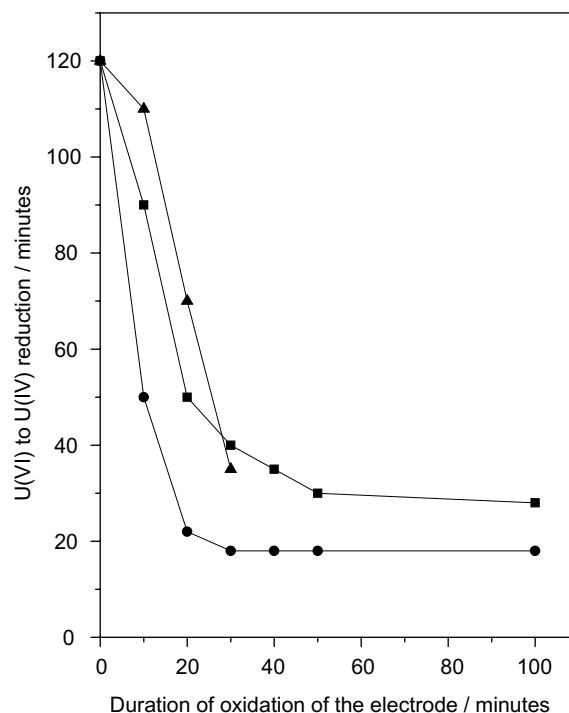


Fig. 6. Activation by galvanostatic anodization and potentiostatic cathodization. Effect of duration of galvanostatic anodization. Platinum wire gauze electrode was anodized galvanostatically at a preselected current for a known period in $1 \text{ M H}_2\text{SO}_4$. Electrode was the potentiostatically cathodized at -0.150 V until current reached background level of $25 \mu\text{A}$ in same electrolyte. An aliquot of U(VI) was added in the same electrolyte and reduced at -0.150 V vs SCE. Key: (■) 1, (●) 2 and (▲) 3 mA.

Table 1. Controlled potential coulometric determination of uranium by successive addition technique using the activated platinum wire gauze electrode

S. No.	Solution aliquot weight /g	Time /min	Charge, Q /C	Blank, Q /C	Uranium content in the aliquot /mg	Concentration of uranium /mg g^{-1}
1	0.08566	16	4.487	0.021	5.508	64.30
2	0.09145	16	4.800	0.021	5.894	64.45
3	0.08926	16	4.689	0.021	5.757	64.50
4	0.09052	16	4.753	0.021	5.836	64.42
5	0.11000	16	5.782	0.021	7.105	64.59
6	0.16180	15	8.469	0.019	10.421	64.41
7	0.12891	15	6.740	0.019	8.289	64.30
8	0.14564	15	7.612	0.019	9.364	64.30
9	0.12973	15	6.777	0.019	8.335	64.24
10	0.13233	15	6.922	0.019	8.513	64.33
11	0.16004	16	8.369	0.021	10.296	64.33
12	0.08148	16	4.279	0.021	5.251	64.46
13	0.06548	16	3.443	0.021	4.220	64.46
14	0.03195	16	1.695	0.021	2.064	64.63
15	0.05101	16	2.692	0.021	3.294	64.59
16	0.12513	16	6.555	0.021	8.058	64.40
17	0.16036	17	8.392	0.022	10.323	64.37
18	0.17450	17	9.136	0.022	11.240	64.41
19	0.18831	18	9.850	0.023	12.120	64.36
20	0.20850	18	10.910	0.023	13.427	64.40

Mean U concentration: $64.41 \text{ mg U g}^{-1}$.

Expected U concentration: $64.37 \text{ mg U g}^{-1}$.

Standard deviation: 0.10 mg U g^{-1} .

Relative standard deviation: 0.16% .

solution electrolyte is inversely proportional to the active electrode surface area. The decrease in the period of reduction of U(VI) confirms the enhancement in the active area as the number of successive potentiostatic A–C cycles is increased.

(b) *Galvanostatic anodization–potentiostatic cathodization*. Alternatively, anodization of the electrode was also carried out at constant currents of 1, 2 and 3 mA, in independent experiments, in 1 M H₂SO₄ followed by reduction of the oxides at the controlled potential of –0.150 V in the same electrolyte. Reduction of U(VI) was carried out in the same electrolyte after the reduction of oxides. The results are shown in Figure 6. It is seen that the behaviour of the electrode towards the galvanostatic anodization is similar to that for potentiostatic anodization. Enhancement in the surface area of the electrode was observed as the duration of anodization increased. A plateau is reached after 20 min for different anodization currents. Anodization at 2 mA for 30 min produced the maximum achievable enhancement in active surface area.

4. Determination of uranium by successive addition technique employing the activated electrode

The results of determination of uranium by successive addition are shown in Table I. Precision (RSD) and accuracy of ±0.2% were obtained for uranium in the range 5 to 10 mg. Also, U concentration values were found to be in good agreement with those expected.

The enhanced activity of the electrode remained unaffected on carrying out successive determinations. However, deterioration of the enhanced activity was observed on ageing.

5. Conclusions

A significant enhancement in the catalytic active surface area of a platinum wire gauze electrode was obtained by hybrid chemical and electrochemical treatments. This allowed the reduction of U(VI) to U(IV) quantitatively with 100% current efficiency at –0.150 V vs SCE in 1 M H₂SO₄ within 15 to 18 min. Uranium determination could be carried out by primary coulometry. The precision and accuracy obtained were better than 0.2% at levels of 5 to 10 mg.

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