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Two Types of Potential Oscillation During the Reduction of Dichromate on Gold Electrode in H₂SO₄ Solution

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(Dated: Received on March 18, 2005; Accepted on July 22, 2005)

Two different types of potential oscillations have been identified for the first time during dichromate reduction on a gold electrode in a solution of dilute sulfuric acid. One occurs before hydrogen evolution due to the formation and dissolution of passivating films of low-valence chromium oxides, and the other generates, accompanying periodic hydrogen evolution, from the coupling of electrochemical reactions with diffusive and convective mass transport. More interestingly, these two types of oscillations correspond to two crossing loops in the cyclic voltammogram (CV). Such a relation of oscillations with crossed CVs will provide a new way to find electrochemical oscillatory systems systematically and rapidly.

Key words: Potassium dichromate, Gold electrode, Reduction, CV criterion, Potential oscillations

I. INTRODUCTION

Since the first report on current oscillations in the polarographic reduction of chromate by Frumkin and co-workers [1], this oscillatory reduction system has attracted interests of some researchers [2-4]. Fleszar *et al.* studied current oscillations during the reduction of Cr₂O₇²⁻ on a dropping mercury electrode (DME) [3]. Franczak *et al.* investigated current oscillations on a hanging mercury drop electrode (HMDE) in K₂Cr₂O₇ solutions with acetic acid and acetate buffers, and they related the oscillations to the formation and dissolution of Cr(OH)₃ films [4]. Jiang and Pletcher observed current oscillations on a rotating Ni disk electrode in a solution of 50 g/L CrO₃+2 g/L H₂SO₄, and they also attributed the oscillation to the passivating film formed periodically [5,6]. The dynamic behavior of the electrode-film-electrolyte structure can manifest potential oscillations as well during Cr(VI) reduction under galvanostatic conditions in electrolyte solutions containing TiF₆²⁻ or F⁻ [7].

Till now, both current and potential oscillations reported were ascribed only to the surface processes, i.e. periodic formation and dissolution of cathodic films. In this paper, we present for the first time two different types of potential oscillations (named type I and II), correlative to two crossing loops in the CV during the reduction of dichromate on a gold electrode in dilute sulfuric acid. Surface processes and mass transport play the key role, respectively, in the two types of oscillations.

II. EXPERIMENTAL SECTION

Electrochemical experiments were carried out with a CHI 660A Electrochemical station (CH Instrument Inc., USA). A gold disk (2 mm in diameter), a platinum wire and a saturated calomel electrode (SCE) were used as the working, counter and reference electrode, respectively. The working electrode was polished with sand paper and then cleaned with ultrasonic waves, followed by electrochemical cleaning in the background solution (1 mol/L H₂SO₄) until repeatable cyclic voltammograms were obtained. Raman spectra were obtained with a Renishaw RM1000 confocal microscope. The exciting wavelength was 632.8 nm from an He-Ne laser with a power of ca. 3 mW on the sample. A self-designed spectroscopic cell was used, which was made by Teflon with a quartz window. More details on the instrument and the cell can be found elsewhere [8]. All solutions were freshly prepared with doubly distilled water and analytical grade chemicals.

III. RESULTS

A. CVs and *insitu* Raman spectroscopy

As shown in Fig.1, two closed crossing loops, I and II, appear when the potential scan is reversed at -0.9 V (the dashed line), yet only crossing loop I can be observed while the lower potential limit is set at -0.4 V (the solid line) positive to the hydrogen evolution. By crossing loop we mean that the current for the backward scan is larger than that for the forward scan in a range of potentials. However, these two crossing loops generate from different kinetic processes. It is well known [5,6] that the reduction product of dichromate before hydrogen evolution is not a chromium metal but oxides of

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chromium with intermediate valences, which form passivating films, soluble in acidic solutions. Thus crossing loop I in Fig.1 is from the formation and dissolution of the passivating films, rather than from electrocrystallization of metals as in the electrodeposition of Ni-Mo and Ni-W on the glassy carbon electrode [9,10]. Nevertheless, crossing loop II comes from the depletion (forward scan) and replenishment (backward scan) of the surface concentration of dichromate. The descending branch during the forward scan is a reflection of dichromate depletion near the electrode surface through reduction under diffusion control, because a limiting diffusion current plateau occurs at a slower potential scan.

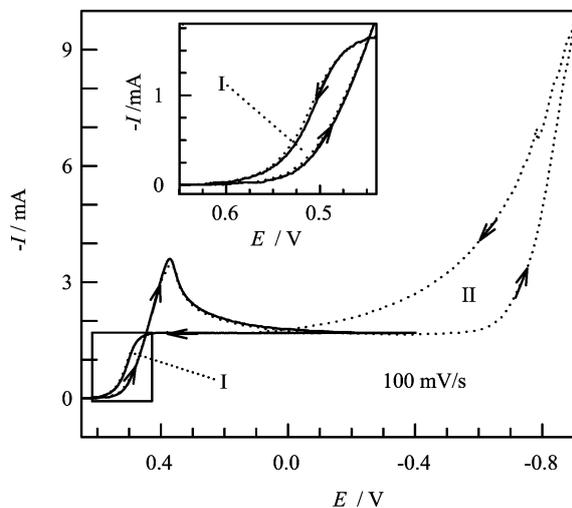


FIG. 1 Cyclic voltammograms on the gold disk electrode in 0.2 mol/L H_2SO_4 solution containing 0.1 mol/L dichromate with (dotted line) and without (solid line) hydrogen evolution. The insert is an enlargement of crossing loop I.

The surface concentration distribution of dichromate (Fig.2) measured by an *insitu* spatial-resolved Raman spectroscopic technique clearly shows a diffusive pattern. The Raman spectra were obtained by progressively changing the distance between the laser focus and the working electrode surface. The larger reduction current during the backward scan results from the enhanced convective mass transport of dichromate induced by hydrogen evolution because crossing loop II disappears without hydrogen evolution (the solid line in Fig.1). This convective flow can restore the surface concentration of dichromate and raise the current over the stationary limiting reduction current of dichromate for a moment before it depletes again. It is noticing that the reverse current at ca. -0.6 V where hydrogen evolution stops is as large as the peak value of dichromate reduction.

We have found that a crossing loop in the cyclic voltammograms is a common characteristic for electrochemical oscillatory systems, and it can act as a

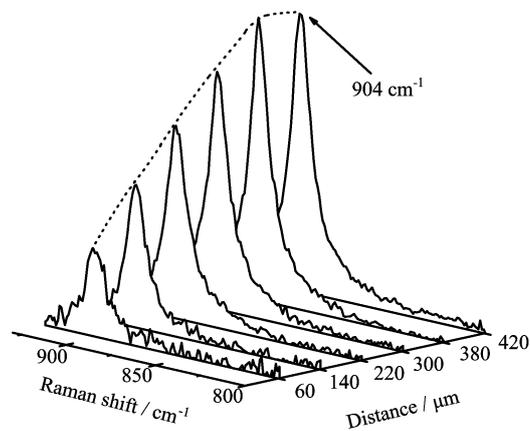


FIG. 2 Spatial-resolved *insitu* Raman spectra at 0 V on the gold disk electrode in 1 mol/L H_2SO_4 solution containing 0.2 mol/L dichromate. The exposure time for CCD is 50 s. The dotted curve lying at peak 904 cm^{-1} indicates the dichromate concentration profile in the diffusion layer.

useful criterion for electrochemical oscillations [11,12]. The crossing loop means that there are a pair of positive and negative feedbacks overlapped between the bistable states. In order to oscillate in two stable states, self-enhancing and self-repressing processes should co-exist, and predominate alternatively, so that the system is able to move to and fro between the two states. Some other characteristics, such as NDR/HNDR, N-/S-shaped steady-state $I-E$ curves, and autocatalysis, were also related to electrochemical oscillations [13,14]. However, the information from these characteristics is apparently limited since they mainly involve “one-way” between the two stable states. In contrast, CV can provide us with “two-way” information by simply scanning the potential forward and backward in a wide range within one or two minutes. We also convincingly proved that with lots of experimental facts [11,12,15-17] this CV-based criterion has a wider range of applications than the impedance-based one. For example, Neither the impedance spectra nor the N-shaped $I-E$ curve in the forward potential scan could include the feedback information of convection mass transfer induced by the hydrogen evolution as the crossed CV does (crossing loop II in Fig.1).

According to our CV-based criterion, two different types of oscillations could be expected to take place, corresponding to the two crossing loops. The prediction proves to be true, i.e. two different types of potential oscillations appear both under current scan (Fig.3 (a)) and under constant current control (Fig.3 (b) and (c)). To our knowledge this is a first observation on two types of potential oscillations during the dichromate reduction on gold electrode in dilute sulfuric acid. Especially, they were found simply through the CV-based criterion.

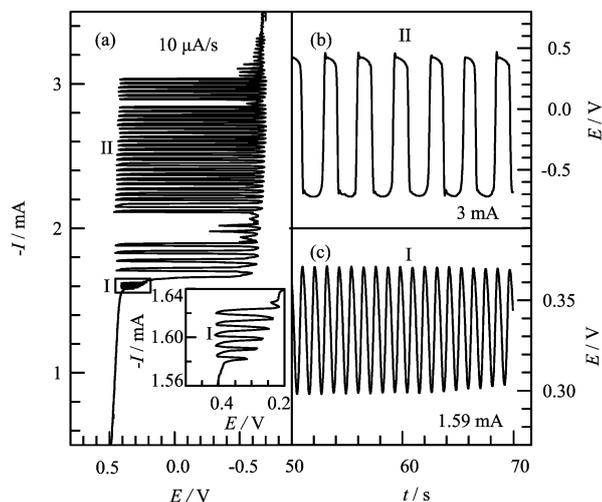


FIG. 3 Potential oscillations on the gold disk electrode in 0.2 mol/L H_2SO_4 solution containing 0.1 mol/L dichromate during (a) current scan and under (b)-(c) constant current control. The insert in (a) is an enlargement of oscillation I.

B. Oscillatory mechanisms of type I and II

The potential oscillations of type I appear early before hydrogen evolution during the current scan with smaller amplitudes, and this type of oscillations can be associated with the crossing loop I in Fig.1. So the reason for this type of oscillations is the same as the corresponding crossing loop, namely coupling of charge transfer with formation and dissolution of passivating films.

The potential oscillations of type II mainly stem from the coupling of charge transfer with diffusion and convection mass transport. Typically, the oscillation accompanying periodic hydrogen evolution can appear only above the limiting diffusion current and the oscillatory amplitude is within the limiting current plateau range. While the applied current is larger than the limiting diffusion current for dichromate reduction, its surface concentration soon depletes to zero owing to the limited supplying rate by diffusion. In order to maintain the applied current, the potential moves to the lower potential side of the plateau till hydrogen evolution takes place. The growth, detachment and movement of the hydrogen bubbles produce forced convection mass transport. Then the surface concentration of dichromate is replenished and the potential moves back to the higher side of the plateau again, where only the reduction of dichromate can occur and hydrogen evolution is thus repressed completely. Then the relaxation process of the surface concentration of dichromate starts again and new cycles repeat. Unlike the oscillations of type I, a constant agitation of solution or rotation of electrode immediately stops the oscillation of type II, and the potential stays at the positive side, because no

depletion can occur in this case with a constant convective flow. This fact also indicates that, in addition to the depletion, alternately predominant convection from the periodic hydrogen evolution is essential, too, for the oscillations of type II.

IV. DISCUSSION

A. The crossed CV

Someone may argue that why we observed many oscillations without observing a crossed CV? We would say that the appearance of crossed CVs depends on the potential sweep range and potential scanning rate [12]. We also give such a case in Fig.1 where crossing loop II does not appear by reversing the potential scan at -0.4 V before hydrogen evolution (the solid line). Nevertheless, we certainly could not conclude in this case that oscillations of type II could occur without a crossed CV. Note that this CV loses some important information for oscillations of type II: (i) one of the two states, i.e. dichromate reduction accompanying hydrogen evolution (the other state, i.e. dichromate reduction without hydrogen evolution), and (ii) one of the two feedbacks, i.e. replenishment of dichromate through convection mass transport (the other feedback, i.e. depletion of dichromate by reduction under diffusion control). Since oscillations involve periodic hydrogen evolution, the CV must also contain the hydrogen evolution reaction. In a word, to describe the oscillations by the crossed CV the potential scan range should be wide enough to contain all reactions involved in the oscillations. What we need to do in this example is simply to extend the scan range of potential, say to -0.9 V (the dotted line of Fig.1).

On the other hand, if we scan the potential very slowly in nearly a steady-state manner as did in the literature, crossing loops might be not observable either simply because oscillations are not a steady-state. Experimentally, a potential scan rate of 100 mV/s works well and is chosen for all of our previous and present work, including reductions of anions and cations, electrocatalytic oxidations of small organic molecules, and electrodisolution of metals [8,11,12,15-17]. Qualitatively, such a potential scan rate is fast enough to catch the positive and negative feedback kinetic behavior of oscillatory systems with a oscillation period of (sub)seconds. It can be illustrated also by the example of crossing loop II. As we know that (i) the convective mass transport is stronger at lower potentials with more hydrogen evolution, and (ii) the convective flow near the surface vanishes soon in a few seconds after hydrogen evolution stops. So, if we reverse the potential scan to the positive side fast, the information of larger strength of convective mass transport at a lower potential can be still caught at a higher potential, even after hydrogen evolution disappears. That is why the current for the

backward scan is larger than that for the forward scan in crossing loop II with a fast potential scan. Such a convective feedback near the electrode surface can hardly be shown with a very slow potential scan because its strength fades away rapidly.

Furthermore, at this rate of potential scan the size of crossing loops can be still adjusted by other experimental parameters such as concentration, pH, temperature and so on, in order to match the positive and negative feedback strength properly for oscillations. Generally, a larger crossing loop is favorable to oscillations, which implies that both negative and positive feedbacks are strong enough to drive the system forth and back. This is a practical way to optimize the oscillatory condition by the crossed CV.

B. Oscillatory modeling

Oscillatory models concerning formation and dissolution of passivating films during metal electrodisolution have been made by many researchers [18]. For example, Franck and FitzHugh developed one of the earliest quantitative models for iron electrodisolution in H_2SO_4 with two differential equations in terms of the over-potential E and the surface coverage θ [19]:

$$\frac{dE}{dt} = k_1 - k_2E - k_3\theta + k_4EW(E, \theta) \quad (1)$$

$$\frac{d\theta}{dt} = k_5EW(E, \theta) \quad (2)$$

where $W(E, \theta) = \theta + (1 - 2\theta)H(E)$, and H is the Heaviside step function. This basic discontinuous model was further modified with many other forms [18]. These models can be applicable in principle to the oscillations of type I in this work, and we do not want to repeat them here.

However, little work has been done concerning the coupling of electrochemical reactions with diffusion and convection mass transfer. A simple mathematical model of one dimensional (x) diffusion-convection equation is proposed here to describe the concentration (c) variation of dichromate near the surface during the galvanostatic potential oscillation by reduction under diffusive control and by convective flow induced through hydrogen evolution, respectively:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} \quad (3)$$

where the convection term $-v_x(\partial c/\partial x)$ is correlative to the hydrogen evolution rate $f(r_H)$, and its exact express is difficult to be obtained. For simplicity, the Heaviside step function H is adopted, and we have $f(r_H) = k(x)c^0H(E_H - E)$, which means that convection effect only appears while the potential E becomes lower than E_H for hydrogen evolution ($E_H - E > 0$, $H = 1$;

$E_H - E < 0$, $H = 0$) with the concentration depletion of dichromate in the diffusion layer. The Heaviside step function, although oversimplified, can qualitatively reflect the periodic convection mass transfer from the periodic hydrogen evolution. Eq.(3) can be expressed as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + k(x)c^0H(E_H - E) \quad (4)$$

Eq.(4) can be transformed into the dimensionless form and solved numerically by a finite difference method as outlined in Ref.[20] with

$$c(x, 0) = c^0, \quad \lim_{x \rightarrow \infty} c(x, t) = c^0 \quad (5)$$

and under galvanostatic control

$$i = nFAD \left[\frac{\partial c(x, t)}{\partial x} \right]_{x=0} \quad (6)$$

$k = 12.5 \exp(-x/0.00496)$, which is deliberately chosen so that the dichromate concentration in the diffusion layer can be restored to nearly c^0 (not exactly, with a relative error about 1%), while the potential is less than E_H within a time interval of 0.08 s for next iteration. Such a choice of k is rational because the convection strength from the hydrogen evolution attenuates with the increase of distance x . Since the reduction is diffusion-limited, the concentration variation of dichromate near the surface can be transferred into the potential variation via the well-known Nernst equation regarding the relationship of potential with reactant concentration.

Figure 4 shows the numerical results of Eq.(4), which qualitatively reproduces the galvanostatic potential oscillations of type II in Fig.3 (b).

V. CONCLUSIONS

Two different types of potential oscillations were found by cyclic voltammograms. Type I results from the coupling of charge transfer with formation and dissolution of passivating films, and type II from the coupling of charge transfer with mass transport of diffusion and convection.

We believe that the crossed CV will provide a new way to find more electrochemical oscillators systematically and rapidly. A larger number of other new electrochemical oscillators discovered in this way recently in our group will be reported soon in a series of papers followed.

VI. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.20073012, 20373063).

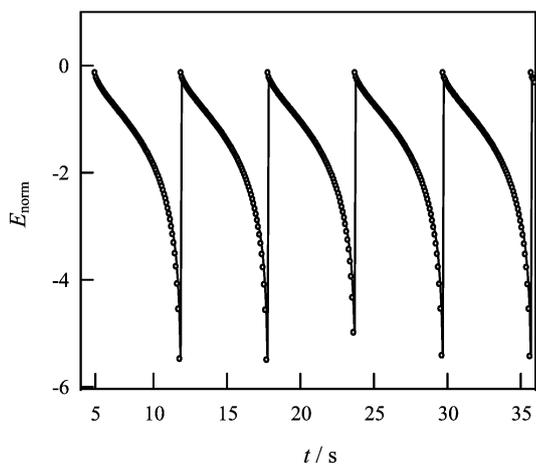


FIG. 4 Numerical potential oscillations from Eq.(4) with three dimensionless parameters: (1) dimensionless diffusion coefficient $D_M=(D\Delta t)/(\Delta x^2)=(5\times 10^{-6}\times 0.08)/0.001=0.4$, (2) dimensionless current $Z=(it_k)/(nFAD^{1/2}c^0)=1.5$, and (3) dimensionless potential $E_{\text{norm}}=[nF(E-E^{0'})]/(RT)=\ln(c/c^0)$. Hydrogen evolution potential $E_{\text{norm}}(H)=-5$, $k=12.5\times \exp(-x/0.00496)$. A cycle in the curves indicates a step of iteration with a time interval of 0.08 s.

Raman spectra were measured in the Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Zhejiang Normal University, Jinhua, China.

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