Oscillations and period-doubling bifurcations in the electrochemical oxidation of thiourea

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Abstract

The electrochemical oxidation of thiourea on a Pt electrode was found to exhibit both simple and period-doubled oscillations. Measurements of the potentiostatic $I/\emptyset$ behavior and impedance spectra suggest that the studied system belongs to the hidden negative differential resistance (HNDR) oscillator. The dependence of complex oscillations on initial compositions of the reaction mixture and temperature has also been characterized, which showed that: (1) lowering the reaction temperature facilitates the occurrence of complex oscillations; (2) the frequency of oscillation increases linearly with respect to the temperature; and (3) hydrochloric acid exhibits stronger influence on the reaction behavior than nitric acid.
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1. Introduction

The oxidation of sulfur compounds has been known to be capable of exhibiting various nonlinear phenomena [1–11]. For example, recent studies have shown that the oxidation of thiourea can exhibit complex periodic oscillations and chaos, the coexistence of two stable steady states and traveling waves [1–3]. The capability of supporting such rich dynamical behavior has made the oxidation of thiourea an attractive model system for the understanding of nonlinear chemical kinetics. Earlier studies have suggested that oxidants may have played an essential role in resulting chemical oscillations in the sulfur-based oscillators including the oxidation of thiourea [4]. However, very recent studies, particularly the observation of pH oscillations during the oxidation reactions of sulfur compounds, suggest that sulfur chemistry is responsible for oscillations in those sulfur-based oscillators [5–8].

In this study we use an electrochemical method rather than a reagent to oxidize thiourea. The study of the oxidation of thiourea via electrochemical methods has attracted a great deal of attention in the last two decades [14–17], because thiourea has been widely used, for example, as a leveling agent and as an inhibitor in metal corrosion [12,13]. These earlier studies suggest that c,c'-dithiodiformamidinum ion is formed by the reaction at the applied voltage around 0.5 V and at higher voltages the hydrolysis product of c,c'-dithiodiformamidinum ions undergoes further oxidation. Despite numerous studies on the electrochemical oxidation of thiourea, nonlinear phenomena such as oscillations have not been reported in such a system. In this study, the electrochemical oxidation of thiourea was conducted in an acidic environment. Surprisingly, the presence of hydrochloric acid (or nitric acid) makes the electrochemical oxidation of thiourea becoming a new electrochemical oscillator [18–20]. Not only simple but also period-doubled oscillations were achieved when the applied voltage was adjusted as a control parameter.

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2. Experimental

All experiments presented here were conducted in a single cell reactor thermostated through a circulating water bath (±0.1 °C, Polyscience Instrument). The volume of the reactor was 40 ml. The working electrode was a platinum disk electrode with a diameter 2 mm. Before its usage, the working electrode was polished with fine alumina powder (0.05 um) and then rinsed repeatedly with deionized Milli-Q water. The counter electrode was a platinum wire and the Ag|AgCl electrode (CH Instrument) was used as the reference electrode. All electrochemical experiments were carried out with a CHI 660A Electrochemical Station (CH Instruments, INC., USA).

All reagents used in this study were analytical grade. Thiourea, KCl, NaNO$_3$, HCl and HNO$_3$ solutions are prepared by dissolving proper amount of reactants in the deionized water (Ultrafiltered from millipore-Q system). Thiourea solution was prepared on daily basis. Concentrations of hydrochloric acid and nitric acid solution were determined by titrating the solution with standard Na$_2$CO$_3$ solution.

3. Results and discussion

Fig. 1 presents a typical experimental observation of the cyclic voltammogram of 0.02655 M thiourea in 0.5416 M nitric acid solution, in which the scanning speed is 0.001 V/s, much slower than that used in regular cyclicvoltammetry experiments. No external resistor is used in this study. The slow scanning makes the applied voltage function like a bifurcation control parameter, similar to the initial concentration of reactants in a closed reaction system. As shown in the figure, when the scanning potential is increased from −0.2 V, current quickly reaches a constant value near zero, implying that there is no reaction activity during that stage. When the applied potential is increased to 0.8 V, current decreases again and tends to reach another plateau. Surprisingly, oscillatory behavior appears when the applied voltage, V, becomes larger than 0.5 V. Because oscillations develop smoothly from the steady state, a supercritical Hopf-bifurcation occurs here [18]. According to earlier investigations [14–17], when the applied voltage is larger than 0.5 V, thiourea are oxidized to form $[(NH_2)_2CS]_2^{2+}$, S, SO_4^{2-}, etc. The phenomenon that current oscillates around a plateau indicates that mass transportations near the platinum electrode is a limiting factor.

The forward scanning process is stopped at the voltage 1.4 V in this experiment. However, the above oscillatory behavior will continue if the upper voltage is
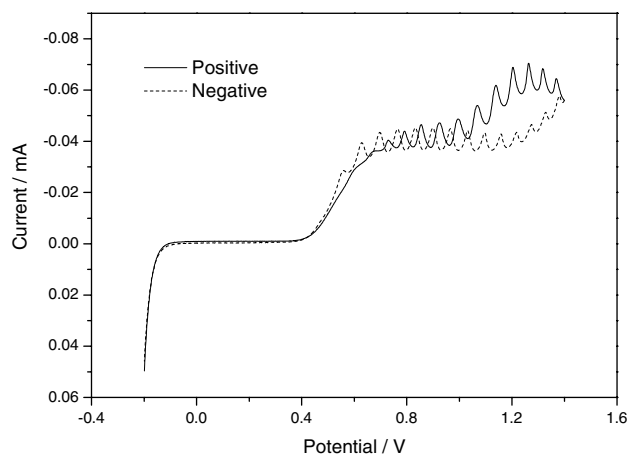

Fig. 1. Voltammogram of 0.02655 M thiourea in 0.5416 M HNO$_3$. There is no external resistor in this study. The scan rate is 0.001 V/s. The solid and dashed lines represent, respectively, the positively and negatively scanned current responses. The reaction temperature is 20.0 ± 0.1 °C.

increased further, for example, up to 1.7 V. When scanning the potential in the negative direction (see the dashed line), oscillatory process continues until a critical voltage is passed, i.e. ca. 0.5 V. The formation of a crossed current–votammogram cycle implies that there exists a feedback loop [21].

Fig. 2 presents the influence of the applied voltage on the behavior of the electrochemical oxidation of thiourea. Here, concentrations of thiourea and HNO$_3$ were kept constant at 0.0265 and 0.5416 M, respectively. The applied voltage, V, was adjusted gradually from 0.7 to 1.4 V. When the applied voltage is larger than 1.4 V, the production of oxygen becomes significant and therefore the maximum applied voltage characterized in this study is 1.4 V. Fig. 2a presents the time series of oscillations in current collected at the voltage 1.1 V, in which the current oscillates between −0.038 and −0.048 mA. Qualitatively the same behavior has been obtained when other voltages (i.e. 0.8, 1.2, and 1.4 V) were used. Although oscillations become slightly irregular when the applied voltage is adjusted, no further bifurcations could be obtained in this system. Other properties of the periodic oscillation such as the frequency and amplitude are summarized in Fig. 2b. As shown in the figure, the variation of the oscillation frequency is not monotonic and a maximum is achieved at 1.0 V. Similar scenario happens to their amplitudes too, which are denoted by triangles.

In the thiourea–nitric acid system, a small amount of crystals often appear on the surface of the working electrode several hours after the beginning of the reaction. IR analysis indicates that the crystal consists of $((NH_2)CS)_2(NO_3)_2$. The formation of crystals causes a slow, but continuous drift in the oscillating current and eventually leads to damped oscillations. Our study illustrates that the formation of crystal becomes partic-
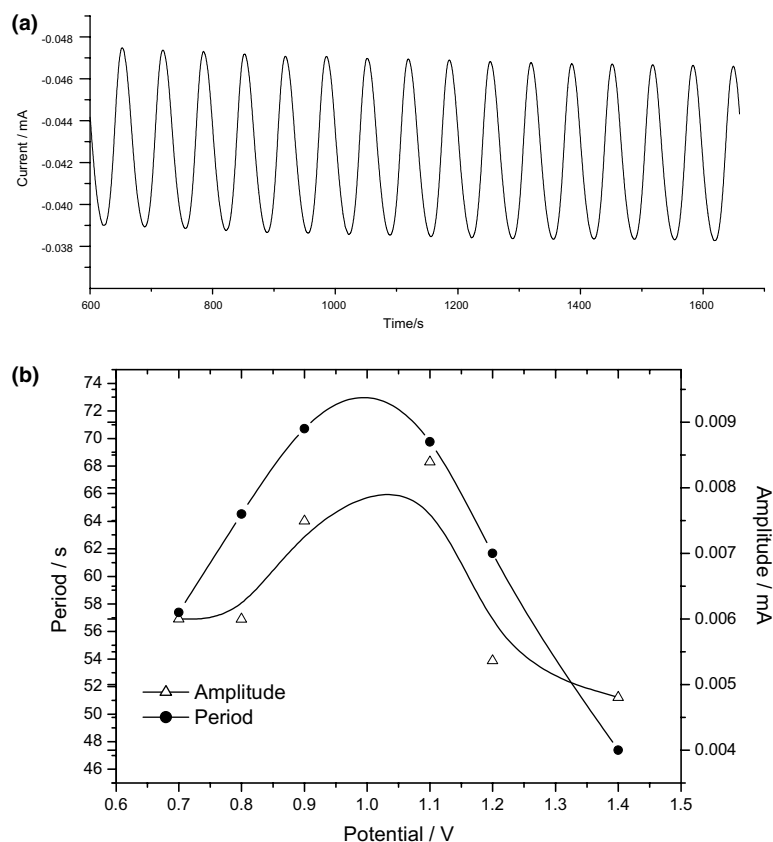
Fig. 2. (a) Time series of anodic current oscillations during the electrochemical oxidation of thiourea, and (b) Variations of the amplitude and frequency of oscillation as a function of the applied voltage. Initial compositions of the system are [HNO$_3$] = 0.5416 M, [thiourea] = 0.02655 M, and T = 20.0 ± 0.1 °C.

ularly prominent at low reaction temperature. In order to characterize the effect of reaction temperature on the electrochemical oxidation of thiourea, a new system, i.e. thiourea–hydrochloric acid, is used in the following experiments. In comparison with the thiourea–nitric acid medium, the thiourea–hydrochloric acid system does not form visible amount of crystal and yields stronger signal (i.e. larger amplitudes) and thus has better signal to noise ratio. Another important advantage of the thiourea–hydrochloric acid system is its stability, in which oscillations could last for several hundreds hours and be reproduced very well.

The influence of the concentration of hydrochloric acid on the above electrochemical oscillations is shown in Fig. 3, in which the concentration of hydrochloric acid is varied as (a) 3.1955 M, (b) 2.1788 M, (c) 0.1887 M and (d) 0.09383 M. The applied voltage is kept at 0.8 V, the same as that used in Fig. 2a. The reaction temperature is 5.0 ± 0.1 °C. Concentrations of other reagent are [KCl] = 0.30 M and [thiourea] = 0.1993 M. The addition of KCl is desired to improve the conductivity of the reaction solution, which becomes particularly important at low hydrochloric acid concentrations. In Fig. 3a, only simple

one-peak-per-period oscillations are observed. The period of oscillation is about 100 s. When hydrochloric acid concentration is decreased, a small peak appears between two consecutive large peaks, leading to the occurrence of period-2 oscillations (see Fig. 3b). If the concentration of hydrochloric acid is decreased still, a transition from period-2 to period-4 oscillations takes place. Eventually, simple one-peak-per-period oscillations are restored via reverse period-doubling bifurcations when hydrochloric acid concentration is reduced to 0.09383 M (see Fig. 2d). The above result illustrates that the concentration of hydrochloric acid is an effective bifurcation control parameter.

The reaction temperature is also found to exhibit significant influences on the electrochemical oxidation of thiourea. In general, decreasing the temperature favors the occurrence of complex oscillations. For example, period-4 oscillations shown in Fig. 3c become simple one-peak-per-period oscillations when the reaction temperature is raised to above 20.0 °C. However, at low temperature, it takes very long time for the system to reach a stable oscillatory state. At −2.0 °C, for instance, the observed oscillations are still transient after more
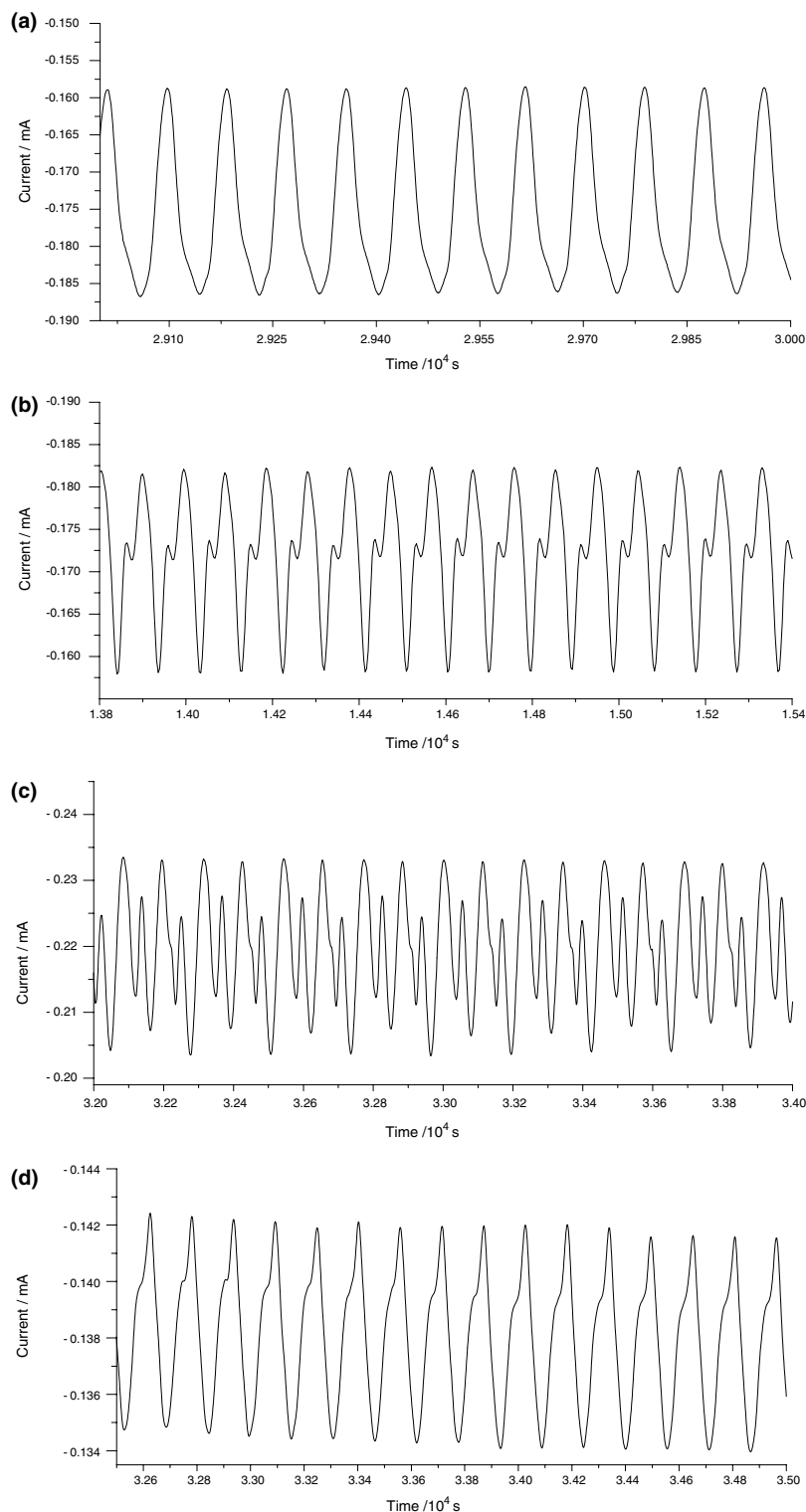
Fig. 3. Electrochemical oscillations under different initial concentrations of HCl: (a) 3.1955 M, (b) 2.1788 M, (c) 0.1877 M, and (d) 0.09383 M. The reaction temperature $T = 5.0 \pm 0.1$ °C and the applied voltage is 0.8 V. [thiourea] = 0.1993 M, [KCl] = 0.3 M.

than 100 h. Fig. 4 summarizes the oscillation frequency obtained under different temperatures, in which a linear function is achieved: $f/\text{Hz} = -0.27745 + 0.00104\ T/\text{K}$, where T represents the temperature. Other reaction conditions are: [thiourea] = 0.1993 M, [KCl] = 0.3 M, and

[HCl] = 2.1787 M. The applied voltage is 0.8 V. Under the above reaction conditions, oscillatory phenomena completely disappear after the reaction temperature is increased to above 35.0 °C and complex oscillations appear when the temperature is below 5.0 °C.
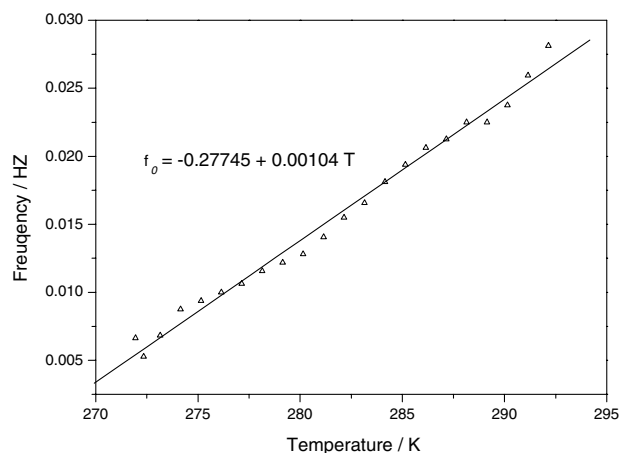
Fig. 4. The variation of the frequency of oscillation with respect to reaction temperature, T. A linear relationship is obtained here. The applied voltage is 0.8 V. [thiourea] = 0.1993 M, [KCl] = 0.3 M and [HCl] = 2.1788 M.

To shed light on the nature of the above electrochemical oscillator, in Fig. 5a we characterized the potentiostatic $I/\emptyset$ behavior, in which a N-shaped curve was obtained. According to the categorization methods suggested by Strasser and co-workers and by Krischer [22,23], the appearance of a N-shaped potentiostatic curve indicates that the studied system belongs to class-III, NDR oscillators, or class-IV, HNDR oscillators, where the electrical double layer potential is an autocatalytic variable leading to the negative differential resistance. As shown in the Fig. 5a, for the applied potential smaller than 0.7 V, the stationary – $I/\emptyset$ branch has a positive slope. However, under linear galvanic voltammogram and galvanostatic conditions, oscillations have been observed on this positive – $I/\emptyset$ branch (see Figs. 5c,d), which therefore suggest that the electrochemical oxidation of thiourea is a class-IV, HNDR-type oscillator [22,23]. The above conclusion is further supported by the measurement of the impedance spectrum (see Fig. 5b) at the point (open circle) indicated in Fig. 5a, in which a positive zero-frequency impedance is obtained.

4. Conclusion

This study illustrates that the electrochemical oxidation of thiourea can exhibit both simple and complex nonlinear behavior. As shown in Figs. 3 and 4, both the reaction temperature and the concentration of hydrochloric acid can be used as a control parameter to effectively manipulate the behavior of the electrochemical reaction of thiourea. It is interesting to point out that the influence of the applied voltage depends on the types of acid used: in the HNO_3 system, no significant influence on the oscillatory behavior was recorded when the applied voltage
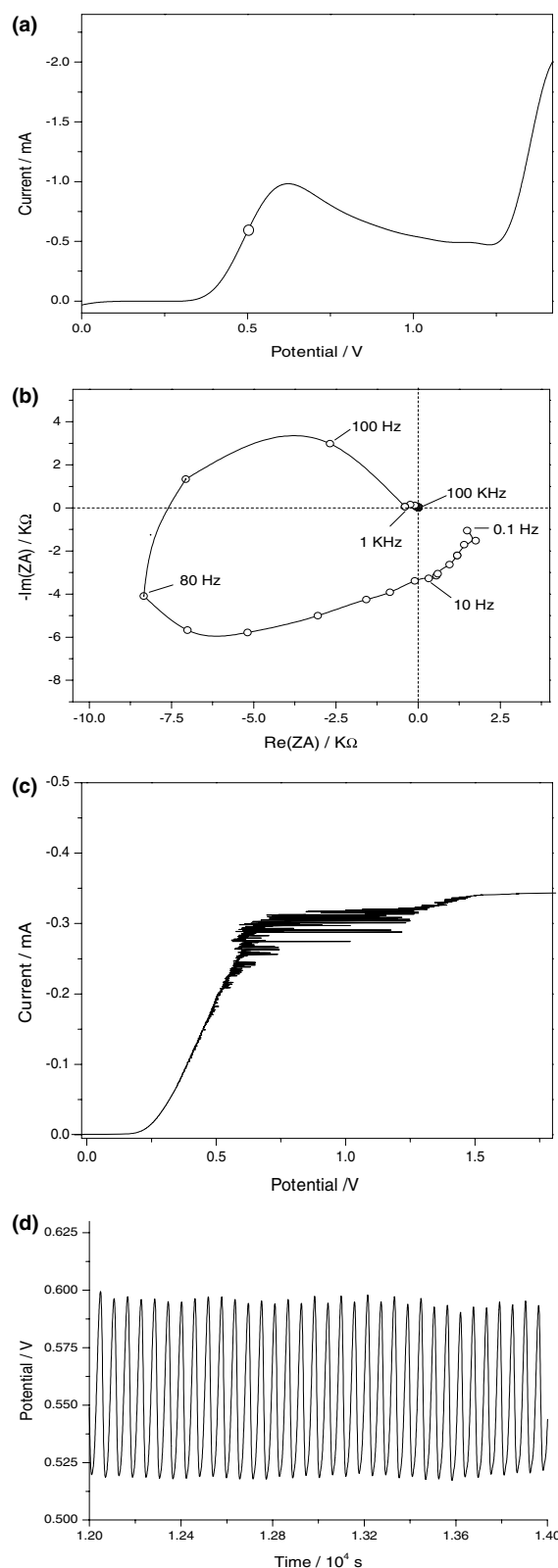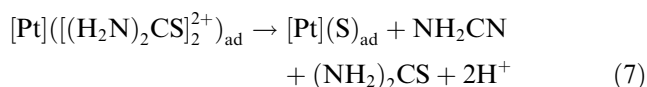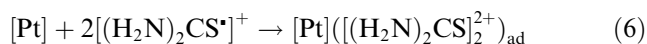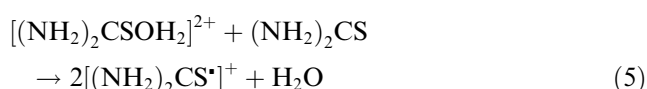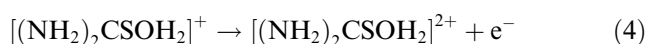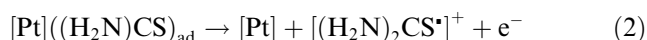

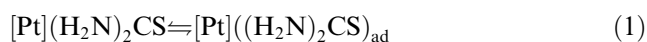Fig. 5. (a) The potentiostatic $I/\emptyset$ behavior, (b) impedance spectrum at the point indicated in (a), (c) linear galvanic voltammogram and (d) potential oscillations under a constant current (I = 0.0003 A). In (a) the scan rate equals 0.1 V/s. In (b) the applied potential is 0.5 V vs AgCl/Cl. The scan rate is 10^{-8} A/s in (c). Reaction conditions are: [HCl] = 1.501 M, [Thiourea] = 0.1993, [KCl] = 0.30 M, and T = 5.0 ± 0.1 °C.

was adjusted between 0.6 and 1.4 V. In contrast, transitions between simple and complex oscillations took place when the voltage was varied in the hydrochloric acid system. The difference caused by NO_3^- and Cl^- ions could be understood based on their absorption properties on the surface of the working electrode, in which the presence of Cl^- can prevent the formation of inert layers on the surface of working electrode.

The characterization of the origin of the above electrochemical oscillations illustrate that the studied system belongs to HNDR-type oscillator, in which the double layer potential is a fast auto catalytic system variable. The underlying chemical cause for the negative regulation remains to be understood. As discussed in the literature [22,23], the ad- and desorptions of the chemicals may play the major role here. For the applied potential larger than 0.5 V, the following reactions are expected to take place [14–17]:

$$[Pt](H_2N)_2CS \leftrightharpoons [Pt]((H_2N)_2CS)_{ad} \qquad (1)$$

$$[Pt]((H_2N)CS)_{ad} \rightarrow [Pt] + [(H_2N)_2CS^\bullet]^+ + e^- \qquad (2)$$

$$[(H_2N_2)CS^\bullet]^+ \xrightarrow{H_2O} (NH_2)_2CSOH_2]^+ \qquad (3)$$

$$[(NH_2)_2CSOH_2]^+ \rightarrow [(NH_2)_2CSOH_2]^{2+} + e^- \qquad (4)$$

$$[(NH_2)_2CSOH_2]^{2+} + (NH_2)_2CS$$
$$\rightarrow 2[(NH_2)_2CS^\bullet]^+ + H_2O \qquad (5)$$

$$[Pt] + 2[(H_2N)_2CS^\bullet]^+ \rightarrow [Pt]([(H_2N)_2CS]_2^{2+})_{ad} \qquad (6)$$

$$[Pt]([(H_2N)_2CS]_2^{2+})_{ad} \rightarrow [Pt](S)_{ad} + NH_2CN$$
$$+ (NH_2)_2CS + 2H^+ \qquad (7)$$

$$[Pt](S)_{ad} + 4H_2O \rightarrow [Pt] + SO_4^{2-} + 8H^+ + 6e^- \qquad (8)$$

As $[(NH_2)_2CS^\bullet]^+$ plays such an important role in the above reactions, in which the sum of reactions (3)–(5) leads to the net reaction $[(NH_2)_2CS^\bullet]^+ + (NH_2)_2CS \rightarrow 2[(NH_2)_2CS^\bullet]^+ + e^-$, its ab- or desorption may also play a major role in establishing the negative regulation. Under higher voltages (>1.2 V), the intermediate product, $[(NH_2)_2CS]_2^{2+}$, will undergo further oxidations [14–17], which consequently create opportunities for more complicated oscillatory behavior to occur.

Acknowledgements

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