Regeneration Oscillation Observed during Oxidation of Methanol, Formic Acid, and Formaldehyde with Chloride Ions

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ABSTRACT
A new type of oscillation, which we name regeneration oscillation, is investigated in detail. The regeneration oscillation is the ordinary potential oscillation with the higher turning potential lower than 0.85 V appearing repeatedly after the potential stays at a value higher than 1.0 V for a long time, of the order of 10 min or an hour. The oscillation has been observed during the oxidation of methanol, formaldehyde, and formic acid at 315 K when their concentrations are high, 1 or 10 mol/L (M), in the presence of high chloride ion concentrations, such as 10^{-2} M, at a current far lower than the maximum current for the appearance of ordinary oscillation. The reason for the appearance of regeneration oscillation has been found by voltammetry and surface-enhanced infrared absorption spectroscopy (SEIRAS).

Keywords : Regeneration Oscillation, Potential Oscillation, Methanol Oxidation, Chloride Ions

1. Introduction
Spontaneous oscillations generated under stationary conditions are intriguing phenomena. The phenomena are observed under far from equilibrium conditions, which are easily achieved in electrochemical systems, namely only by applying a current. Among various types of electrochemical oscillations,1–6 we have been interested in the potential oscillations produced during the oxidation of methanol, formaldehyde, and formic acid in acidic solutions on platinum electrodes.7–9 It is well established10–14 that the framework of oxidation mechanism for these three C1-compounds is a dual path mechanism consisting of an indirect path and a direct path. It is also established14–17 that the indirect path involves adsorbed CO in common for oxidations of the three C1-compounds. It is well known18–22 that adsorbed CO plays a crucial role in the oscillation. Gojuki et al.9 have recently proposed that adsorbed water is also involved in the oscillation.

On the other hand, halide ions are well-known to adsorb on platinum except for fluoride ions.23,24 Sobkowski et al.25,26 have reported that methanol adsorption is completely inhibited with 1 mol/L (M) chloride ions for 6 × 10^{-2} M methanol by using 14C-labeled methanol. Peng et al.27 have shown that the potential for oxidation of CO adlayer positively shifts in the presence of 1 mM chloride ions in a 0.1 M perchloric acid solution. They have also shown that chloride ion adsorption disrupts the interfacial free water structure on top of CO adlayer by surface-enhanced infrared absorption spectroscopy (SEIRAS).

We also found28 that, by adding chloride or bromide ions, hydrogen peroxide reduction produces several new oscillations in addition to the ones found without halide ions.29 Horányi and Inzelt29 investigated the potential oscillation generated by the oxidation of ethylene glycol, glycol aldehyde, and glyoxal in the presence of chloride ions to monitor the surface adsorption state during the oscillation by a tracer method using 36Cl-labeled chloride ions. Although this work did not intend to investigate the influence of chloride ions on the oscillation behavior, it showed that the amount of adsorbed chloride ions increases with an increase in the potential and vice versa during potential oscillation. Chen et al.30,31 have found that the behavior of the potential oscillation generated by formic acid oxidation is drastically changed by adding 5.0 × 10^{-2} M HCl to a solution containing 0.10 M HCOONa and 0.50 M perchloric acid.

We, then, have investigated in detail the effect of chloride ions on the oscillation waveform generated by formic acid and formaldehyde oxidation over a wide range of chloride ion concentrations.32

As a result, a new chaotic oscillation, a very large-amplitude one and others have been found. As for methanol oxidation, this paper describes in detail and discusses potential oscillations, especially regeneration oscillation, in comparison with the oscillations observed during formic acid and formaldehyde oxidation in the presence of wide range of chloride ion concentrations from 10^{-2} to 10^{0} M.

2. Experimental
Details of experimental setup have been described elsewhere.34,35

In short, two kinds of experimental cells were used, an EC cell and an IR cell. The EC cell was for electrochemical measurement with a platinum wire (99.99%, 2.5 cm²) as a working electrode. The IR cell was for electrochemical and infrared spectroscopic measurements with a thin (~50 nm) platinum film (12.4 cm²) as a working electrode, which was deposited on one of the three rectangular faces of a triangular Si prism (20 mm on a side and 25 mm long) by a procedure similar to that described by Miki et al.36 The real surface area was determined by assuming a charge of 0.210 mC/cm² for the monolayer of adsorbed hydrogen on Pt. For both cells, the reference electrode was a reversible hydrogen electrode (RHE) in the supporting electrolyte, 0.5 M sulfuric acid (Wako Pure Chemical Industries, Ltd., Japan, Super Special Grade (SSG)). The counter electrode was a platinumized platinum wire.

A methanol solution with sodium chloride and 0.5 M sulfuric acid was prepared by adding methanol (Wako, SSG), sodium...
chloride (Merck, Suprapur) and sulfuric acid to Millipore “Milli-Q” water. A formic acid or formaldehyde solution was prepared with formic acid (Wako, Special Grade) or paraformaldehyde (Merck, Extra pure) instead of methanol. The solution temperature was set at 315 K (42°C).

Spectra were taken by surface-enhanced infrared absorption spectroscopy (SEIRAS) in the attenuated total reflection mode. They were recorded on an Agilent Technologies Varian 670-IR Fourier transform infrared spectrometer equipped with an MCT detector and a homemade single-reflection accessory. The spectral and time resolutions were 4 cm\(^{-1}\) and 0.24 s, respectively. The reference spectrum was taken at 1.4 V in a methanol, formaldehyde or formic acid containing solution.

3. Results and Discussion

3.1 Regeneration oscillation observed during oxidation of methanol in the presence of chloride ions

Figure 1 shows a potential behavior, where the concentration of chloride ions was 1.0 \(\times\) 10\(^{-2}\) M with 1.0 M methanol. At 50 \(\mu\)A (a) or higher, no oscillation was observed except for a transient oscillation just after the current application. At 20 \(\mu\)A (b), however, a self-excited small oscillation became observed just before a sharp potential rise to approximately 1.1 V, where the potential remained for longer than 3 h and did not show oscillation any more, meaning the cease of oscillation. At 10 \(\mu\)A (c1, c2), a new type of oscillation waveform was observed. After an induction period of approximately 2.5 h, a small-amplitude and short-period oscillation appeared, though irregularly in this case, and then the potential sharply increased to a value higher than 1.0 V (c2), which tempted us to judge that the oscillation ceased. However, after about 3 min, the potential dropped down to approximately 0.20 V and immediately increased to approximately 0.55 V, which was followed by a slow potential increase. After about 1.2 h of monotonous potential increase, the potential began to oscillate again and then sharply rose to approximately 1.1 V again. And after about 5 min, the potential dropped down to approximately 0.20 V and immediately increased to approximately 0.55 V again. The cycle repeated itself to give a new type of oscillation (c1).

We name the oscillation waveform regeneration oscillation because the potential oscillation appears repeatedly after the potential stays at a value higher than 1.0 V, 1.1 V in this case, for a long time, of the order of 10 min in this case. Although the regeneration oscillation may be one of mixed-mode oscillations, it has a distinctive feature that the metastable high potential is higher than 1.0 V, which potential value is a sign of the cease of ordinary oscillations, and the duration of the metastable state is long, sometimes longer than 1 h, as shown later. The regeneration oscillation is similar to the “drastically” changed oscillation observed by Chen et al.\(^{11,12}\) with 5.0 \(\times\) 10\(^{-3}\) M chloride ions and 0.10 M HCOONa in a 0.50 M perchloric acid solution at room temperature, although the duration of the high potential state is very short.

We found that the regeneration oscillation was also observed with 10 M methanol. Figure 2 shows potential behavior when the...
chloride ion concentration was $1.0 \times 10^{-1}$ M with 10 M methanol. At 7.0 µA, no potential oscillation was observed (a), while at 5.0 µA the potential showed five periods of large-amplitude, 0.6 V, oscillations before the potential rose to a value higher than 1.1 V (b), which lasted longer than 40 min. At 3.0 mA, regeneration oscillation was observed (c1, c2). On application of current, a large-amplitude oscillation, regular in this case, immediately appeared for about 1 h, which was followed by a high potential metastable state, lasting for as long as 1.6 h. Then the potential dropped down and immediately a large-amplitude oscillation appeared again. With the passage of time, the duration of large-amplitude oscillation between the two high potential metastable states became shorter from approximately 28 min to a period length of oscillation, approximately 200 s, and probably to zero, meaning no more oscillation appearing, if we had measured the potential longer. This is in contrast to the regeneration oscillation observed at 2.0 µA (d), where the duration of oscillation between the two metastable states seemed hardly to change.

When the concentration of methanol was 0.10 M and that of chloride ions was $1.0 \times 10^{-2}$ M, as shown in Fig. 3, at 3.0 mA the potential showed a fluctuation (a), while at 1.0 mA no fluctuation or oscillation was observed until a sharp potential rise to a value higher than 1.0 V (b). At a very low current, 30 µA, the potential exhibited an oscillation in the potential range between 0.5 and 1.05 V (c). The oscillation waveform has characteristics of ordinary relaxation oscillation with a long period but the higher turning potential, approximately 1.05 V, is close to that of regeneration oscillation. Namely, the oscillation observed here is an intermediate one between ordinary and regeneration oscillations.

Figure 4 depicts the dependence of the occurrence of regeneration oscillation on the chloride ion concentration, [Cl⁻], and on the current, $I_c$, for the oxidation of 10 M methanol at 315 K. We can see that the regeneration oscillation is observed in the chloride ion concentration range between $10^{-3}$ and $10^{-2}$ M. This means that a comparatively high chloride ion concentration is necessary for the appearance of regeneration oscillation but too high a concentration hinders its appearance. It is also known that the chloride ion concentration range above, with decreasing current, first ordinary potential oscillation appears with the higher turning potential lower than ca. 0.85 V. Then regeneration oscillation emerges, which further changes to a potential fluctuation. A diagram similar to Fig. 4 was obtained for 1.0 M methanol, where regeneration oscillation was observed in the chloride ion concentration between $10^{-3}$ and $10^{-2}$ M (not shown). For 0.10 M methanol, oscillations with the higher turning potential higher than 1.0 V like those shown in Fig. 3(c) were observed instead of regeneration oscillation in the chloride ion concentration range between $10^{-4}$ and $10^{-3}$ M.

3.2 Regeneration oscillation observed during oxidation of formic acid and formaldehyde in the presence of chloride ions

To clarify whether or not regeneration oscillation appears during oxidation of formic acid and formaldehyde instead of methanol, we first investigated potential oscillation during formic acid oxidation. Figure 5(a) shows a result with 1.0 M formic acid and 1.0 M chloride ions. A typical regeneration oscillation was observed at 2.0 µA, which is similar to that reported by Okamoto et al. where the higher turning potential was approximately 0.95 V. We found regeneration oscillations in the chloride ion concentration range from $10^{-2}$ to $10^{0}$ M for 1.0 M formic acid.

We then investigated potential oscillation during oxidation of 1.0 M formaldehyde with $1.0 \times 10^{-1}$ M chloride ions. At 40 µA, as shown in Fig. 5(b1), a large-amplitude, larger than 1.0 V, and long-period, approximately 200 s, oscillation appeared, which seemed like a precursor of regeneration oscillation. At 10 µA, after approximately 3.6 h of ordinary oscillation, regeneration oscillation appeared with a decreasing interval from approximately 50 to 20 min (b2, b3). We found regeneration oscillations in the chloride ion concentration range from $10^{-4}$ to $10^{-1}$ M for 1.0 M formaldehyde and with $10^{-3}$ M chloride ions for 0.10 M formaldehyde.

Thus we have found regeneration oscillation during the oxidation of the three C1-compounds. The conditions for the appearance of regeneration oscillation are: (1) the concentrations of the three C1-compounds are high, 1 or 10 M, (2) that of chloride ions is also comparatively high, such as $10^{-2}$ M, depending on the concentration and the kind of the three C1-compounds, and (3) the current is far lower than the maximum current for the appearance of ordinary oscillation but too low a current produces a potential fluctuation. In Section 3.3, we will discuss the mechanism for the appearance of regeneration oscillation using voltammograms and simultaneously measured infrared spectra.
chloride ions at a sweep rate of 10 V/s are current peak numbers and I, II, and IV are current peak notations. Incidentally, peak III is observed at around 1.5 V in the positive-going sweep.1,3,8

Since the potential range for ordinary oscillation is typically between approximately 0.4 and 0.85 V [Fig. 1(c1, c2)], the negative differential resistance (NDR), necessary for the appearance of oscillation, relating to the ordinary oscillation is found on the positive potential side of peak I. However, peak I disappeared at a slower sweep rate of 100 mV/s (b). This is because the increased amount of adsorbed CO due to a slow sweep rate suppresses the methanol oxidation and therefore hides peak I. During ordinary oscillation, the coverage of adsorbed CO is not high, around 0.3,13,20,22 and therefore the NDR should be present like that shown in (a) and produce ordinary oscillation.

When the chloride ion concentration was increased to 1.0 × 10⁻² M (c), where regeneration oscillation appeared, the peak II potential shifted to a value higher than 1.0 V, while the potential, approximately 0.85 V, of a shoulder present on the negative side of peak II (b) remained unchanged. This observation indicates that adsorbed CO remains at a potential higher than 1.0 V, which will be confirmed later by SEIRAS.

To observe the surface adsorption state during the voltammogram measurement, we took SEIRA spectra using an IR cell. The bands changing in intensity with potential in the presence of 1.0 × 10⁻² M chloride ions or higher in the wave number range between 4000 and 1000 cm⁻¹ were found to be the following three bands: linearly bonded CO (CO₁) at 2030–2070 cm⁻¹, bridge-bonded CO (CO₂) at 1800–1860 cm⁻¹, and adsorbed sulfate or hydrogen sulfate at around 1220 cm⁻¹. When the chloride ion concentration was 1.0 × 10⁻² M or lower, an additional band at 1322 cm⁻¹, bridge-bonded formate (HCOO₂) was observed at around 1 V. Since the adsorbed sulfate or hydrogen sulfate band was noisy and increased in intensity only when adsorbed CO disappeared, we focused our attention to CO₁, CO₂, and HCOO₂ bands. Incidentally, OH stretching band at 3600 cm⁻¹ of non-hydrogen-bonded water molecules co-adsorbed with CO₁ was observed in the absence of chloride ions, but it was not observed in the presence of 1.0 × 10⁻⁴ M chloride ions or higher. A similar result has been obtained by Peng et al., who have observed the interfacial free water coverage decreases by a factor of ca. 1/4 with 1 mM chloride ions during oxidation of adsorbed CO formed from CO₂ gas.

The voltammogram for the oxidation of 10 M methanol in the presence of 1.0 × 10⁻³ M chloride ions using an IR cell was a little different, as shown in Fig. 7(a1), from that observed using an EC cell [Fig. 6(c)] under the same experimental conditions. In particular, a broad peak II was observed instead of a shoulder and a comparatively sharp peak II. This is probably due to an averaging of potential gradient present in a thin film electrode. Although the current peak II was broad, we can see in Fig. 7(a2) that adsorbed CO was still present at 1.2 V, a potential higher than the peak II potential [Fig. 6(c), Fig. 7(a1)]. This is in contrast to the case with lower

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**Figure 5.** Oscillation waveforms during oxidation of 1.0 M formic acid with 1.0 M chloride ions at 2.0 µA (a), and 1.0 M formaldehyde ions with 1.0 × 10⁻¹ M chloride ions at 40 µA (b1) and 10 µA (b2, b3). Regeneration oscillation is also observed during formic acid and formaldehyde oxidations.

**Figure 6.** Voltammograms for oxidation of 10 M methanol in the presence of chloride ions at 315 K using an EC cell. (a): 1.0 M HCOOH + 1.0 M NaCl, 2.0 µA (a), two current peaks, peaks I and II, during the positive-going sweep and another, peak IV, during the negative-going sweep were observed. The current peak nomenclature follows the literature
chloride ion concentrations, such as $1.0 \times 10^{-4}$ M with 1.0 M methanol (b1–b4), where adsorbed CO disappeared at a low potential of approximately 1.0 V, which coincided both with the peak II potential and the one for the maximum HCOO$_{B}$ band intensity. The observation is the same as without chloride ions.\(^{42}\)

We can thus say that adsorbed CO is stabilized by the adsorption of chloride ions against oxidation with oxides or hydroxides, although the amount of adsorbed CO is decreased, which is shown by comparing Figs. 7(a2) and (b2). Peng et al.\(^{27}\) and Guillaume et al.\(^{43}\) have reported stabilization of adsorbed CO by chloride ion adsorption. We suppose that the reason for the stabilization is a strengthening of Pt-CO bond by chloride ion adsorption. We suggest that the reason for the stabilization is a strengthening of Pt-CO bond by chloride ion adsorption due to an increase in the electron back-donation from the metal to 2p$^{*}$ orbital of CO.\(^{44}\) This is supported by the fact that the wavenumber of CO$_{L}$ decreased with increasing chloride ion concentrations, e.g., from 2071 to 2054 cm$^{-1}$ at 0.50 V when the chloride ion concentration was increased from $1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$ M with 1.0 M methanol.

We can speculate on the mechanism for the appearance of regeneration oscillation based on the fact that the oxidation of adsorbed CO produces a current shoulder and peak II at different potentials.\(^{[9]}\) The current produces a potential fluctuation. The reason for the appearance of regeneration oscillation has been investigated by voltammetry and surface-enhanced infrared absorption spectroscopy.\(^{40}\) As a result, the peak II potential, around which adsorbed CO is oxidized, shifts to a potential higher than 1.0 V with increasing chloride ion concentration, while a current shoulder observed on the negative potential side of peak II does not. Based on the result, we think that ordinary oscillation appears due to the oxidation of adsorbed CO at around the shoulder potential and regeneration oscillation emerges due to the oxidation of adsorbed CO at around the peak II potential.

4. Conclusions

We have investigated a new type of oscillation, named regeneration oscillation, in detail at 315 K. The regeneration oscillation is the potential oscillation appearing repeatedly after the potential stays at a value higher than 1.0 V for a long time, of the order of 10 min or an hour. The oscillation has been found during oxidation of methanol, formaldehyde, and formic acid. The conditions for the appearance of regeneration oscillation are: (1) the concentrations of the three C$_{1}$-compounds are high, 1 or 10 M, (2) that of chloride ions is also comparatively high, such as $10^{-2}$ M, depending on the concentration and the kind of the three C$_{1}$-compounds, and (3) the current is far lower than the maximum current for the appearance of ordinary oscillation but too low a current produces a potential fluctuation. The reason for the appearance of regeneration oscillation has been investigated by voltammetry and surface-enhanced infrared absorption spectroscopy. As a result, the peak II potential, around which adsorbed CO is oxidized, shifts to a potential higher than 1.0 V with increasing chloride ion concentration, while a current shoulder observed on the negative potential side of peak II does not. Based on the result, we think that ordinary oscillation appears due to the oxidation of adsorbed CO at around the shoulder potential and regeneration oscillation emerges due to the oxidation of adsorbed CO at around the peak II potential.

References