Electrochemical Oscillations during Electro-oxidation of Copper Anode in Phosphoric Acid Solution

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ABSTRACT

This paper reports the occurrence of electrochemical oscillations (EOs) in Cu electro-oxidation of phosphoric acid solution, and systematically investigated the effect of potential, electrolyte composition and concentration, temperature, stirring rate, and scanning speed on EOs. The mechanism of EOs occurred as a result of deposition and dissolution effects of CuH₂PO₄ through electro-oxidation of the Cu anode. The experimental result for amplitude and frequency can be explained by this simplified qualitative analysis, and further verified the previously speculated EO mechanism. This study provides insights into the relevance of micro-chemical mechanisms for the macroscopic non-equilibrium phenomenon and presents novel concepts for highly efficient electrodissolution in metallurgy.

Keywords : Copper Anode, Electro-oxidation, Electrochemical Oscillation (EO), Current Oscillation

1. Introduction

Electrochemical oscillations (EOs) occur in electrodissolution, electropolishing, electrodeposition, and electro-catalytic oxidation of Cu, Fe, Zn, and other metals and their corresponding oxides in electrochemical systems.¹-⁴ Nonlinear elementary reaction steps form in electrochemical systems. As the field gradually drives the system from the equilibrium, the effect of nonlinear terms becomes significant, resulting in EOs and other spatiotemporal phenomena.⁵-⁸

EOs occur on a copper electrode in acidic solutions. Potkonjak et al.⁹,¹⁰ reported the occurrence of current oscillations caused by copper anodic dissolution in trifluoroacetic acid solution. Hai et al.¹¹,¹² found potential oscillations under constant current deposition of copper as a result of the instability of additives.

Three preliminary mechanisms of EOs during copper dissolution were proposed. First, EOs are formed by periodic deposition and dissolution of a material on the electrode surface. Glarum et al.¹³ revealed the occurrence of oscillation in the Cu/H₂PO₄ system. Kamiya et al.¹⁴ indicated that potential oscillation is formed by adsorption of the combined thiocyanate and copper ions on the copper electrode surface. Barkey et al.¹⁵ reported the presence of potential oscillation on a rotating disc electrode or a ring-disk electrode during the constant current electrolysis of copper in sulfuric acid solution containing additives. These oscillation phenomena are due to the deposition and dissolution of the film on the copper electrode surface. Second, oscillations are caused by cyclical changes of intermediate valence ions at the electrode interface. Schaltin et al.¹⁶ found that current oscillation is due to interconversion of Cu²⁺ and Cu⁺ in imidazole ionic liquid-containing copper. Eskhult et al.¹⁷ indicated that alternate synthesis of Cu and Cu₂O nanolayer materials in a solution containing alkaline Cu (II) and citric acid causes current oscillations. Third, oscillations occur when bubbles are generated periodically on the electrode surface; this phenomenon results in periodic variation of gains or losses of the electronic reaction. Mukoyuama et al.¹⁸ detected EO in hydrogen evolution reaction during water electrolysis, which occurs in different types of acids on different types of metals; thus, the mechanism of oscillation is self-catalysis of bubbles at the electrode interface.

The behavior and preliminary qualitative interpretation of factors affecting EOs have been reported previously.¹⁹,²⁰ However, the quantitative description of EO mechanisms in different electrochemical systems still need further investigation.

In this work, the mechanism of periodic current oscillations during Cu electro-oxidation of phosphoric acid solution was systematically studied through experimentation. The origin of oscillations was verified, and the experimental result can be explained by this simplified theoretical qualitative analysis. Furthermore, the results provide a theoretical basis for developing energy-saving techniques in electrochemical systems by analyzing the internal kinetic mechanism that generates EOs.

2. Experimental

Water was purified using a water purification system (PALL Casaeda II I 30, USA). All reagents were of analytical grade. H₃PO₄ was ≥85%.

Electrochemical tests were conducted by PARSTAT PMC1000 electrochemical workstation. For the three-electrode system, the reference electrode was saturated calomel electrode; To simulate industrial electrolysis, the counter electrode was 304 stainless steel sheet (area = 1.0 cm²); the work electrode was copper rod (0.8 mm in diameter, 5.0 mm in length, 99.95% purity). Except for the effective area of the work electrode, the remaining areas were sealed by an insulating polymer to prevent fluctuation in the area during testing. The distance between the work electrode and the counter electrode was 8.0 mm. All electrodes were finely polished and cleaned in acetone and purified water.²¹,²² Electrolytic cell was placed in a heat collector-constant temperature-type magnetic stirrer (DF-101S, Shanghai, China) to maintain the electrolyte at 293 K. Unless specifically noted, the electrolyte contained H₃PO₄ (1.0 mol·L⁻¹), and the scanning speed of the cyclic voltammery was 10 mV·s⁻¹.

HITACHI SU8010, field emission environmental SEM-EDS was used for surface investigation and feature detection. Images and spectra were collected at 20kV accelerating voltage.
3. Results and Discussion

3.1 Current oscillations on the anode

Cyclic voltammetric (CV) experiments were conducted to investigate the electrochemical behavior of Cu anode in 1 mol·L⁻¹ H₃PO₄ solution at 293 K and to determine the potential for the occurrence of current oscillations under potentiostatic conditions. Figure 1a presents the cyclic voltammograms. The red line was acquired from low to high anodic potentials, and the black line was obtained from high to low anodic potentials. The two lines represented the oxidation process. EOs emerged within 1.72–1.95 V in the forward oxidation on the anode in the red line, and EOs emerged within 1.68–1.92 V in the reserve oxidation on the anode in the black line (Fig. 1a). The oscillation range of forward and reserve scanning was almost close; thus, the latter research was mainly focused on forward scanning from low to high potentials. In the forward scan, the ab-section belonged to the active dissolution region. The oxygenation reaction was serious and produced many bubbles. The current density increased gradually and reached the maximum at point b. The current density of the bc-section was stable, and a brown material was formed on the surface of copper anode. The amount of the brown substance increased with increasing potential, and started producing EOs at point c, resulting in the removal of the brown material from the anode surface. With increasing potential, the current value of EOs increased first and then decreased. Finally, EOs disappeared at point d, and the brown material on the surface of the copper electrode fell off completely. In the de-section, the current increased rapidly as the potential moved forward. At point d, the dark red substance was produced on the electrode surface, which reached point e and formed thin layers. The electrochemical chaos occurred in the high voltage region. During the reverse scanning of the ef-section, the dark red substance on the anode surface decreased gradually and showed a bright color on the copper surface at point f. At the same time, the anode surface was obviously electropolished. The production of brown substance on the copper electrode surface and the detection of EO simultaneously occurred during the reverse scanning in the fg-section.

In forward and reverse scanning, the amplitude of current oscillations first increased to a maximum of 1.73–1.78 V, and decreased with further increasing potential. However, the current oscillation was moving ahead on reverse scanning as shown in the inset of Fig. 1a. Figure 1b shows the current-time (I–t) curve at constant-potential of 1.74 V electrolysis (inset is the partially enlarged image).

3.2 SEM analysis of the anode

After testing the I–t curve for 500 s at 1.74 V, the electrode was taken out and dried for SEM and XPS analysis. The particles of various sizes were attached to the partial anode surface, and Fig. 2c shows the particles on the electrode surface exhibited irregular sizes in the range of 200–500 nm. The red box region in Fig. 2b was selected for EDS analysis; the result is shown in Fig. 2b.
inset. The surface material contained C:Cu:O:P with atomic number 34:11:44:11. During testing, C element was a conductive adhesive, and H element was not displayed. Therefore, the material on the surface of the electrode was assumed to be composed of a substance with Cu:P:O 1:1:4.

The peaks at 531.73 and 133.73 eV of the spectra shown in Figs. 2d and 2e, respectively, were attributed to the ortho-phosphate (H$_2$PO$_4^-$) species. Figure 2f shows the XPS spectra of Cu 2p during anode formation. The spectra represented superimposed peaks at 932.49 eV, corresponding to Cu$^{0}$ and Cu$^{+1}$. Based on the above XPS conclusion and the presumed proportion of elements shown in Fig. 2b, it can be further conclude that the deposited material on the electrode surface was CuH$_2$PO$_4$.

3.2 Effect of potential on EOs

In the above systems, time–current (I–t) curves were obtained using the same fresh electrode under a series of different potential values with gradual increase in test potential. The oscillation was first fixed at a constant potential of 1.68 V, resulting in the I–t curve (Fig. 3), which approached a straight line. With further increase in each potential by 0.01 V, the oscillation was noticeable until 1.69 V. Oscillations gradually improved from 1.69 to 1.74 V, and oscillations gradually weakened from 1.74 to 1.85 V in Fig. 3. As shown in CV (Fig. 1), oscillations emerged from 1.72 V and disappeared at 1.95 V. Comparison of Figs. 1 and 3 indicated that the oscillation ranges of the two were slightly different. In CV and I–t curves, the test time for CV was shorter than that for the I–t curve at the same potential, regardless of the same electrode used and the gradual increase of applied potential. Thus, the film formation rate was different from the electrode surface between CV and I–t curve.

Figure 3 summarizes the former 15 s for the I–t curves detected from 1.68 to 1.86 V. Moreover, the law supporting that amplitude and frequency change with increasing potential was obtained from Fig. 4, which shows the frequency of the oscillation strengthened with increasing potential after fixing the same electrochemical system and generating a stable current oscillation. Furthermore, with increasing potential, the amplitude of oscillation increased first and gradually decreased to zero. Comparison of Figs. 1 and 3 indicated that EOs increased before decreasing with increasing potential, illustrating that the conclusions from Fig. 4 was consistent with that of Fig. 1.

3.3 Effect of electrolyte composition and concentration on EOs

The effects of electrolyte composition and concentration on EOs were determined. According to Fig. 5a, oscillation occurred within 0.4–1.1 mol·L$^{-1}$ H$_3$PO$_4$. Figure 5b summarizes the effect of H$_3$PO$_4$ concentration on the oscillating potential range and the maximum current value. As shown in Fig. 5b, the oscillation range of EOs gradually decreased and disappeared with increasing H$_3$PO$_4$ concentration in the oscillation range, and the maximum amplitude of oscillation initially increased and then decreased. At 0.8 mol·L$^{-1}$ H$_3$PO$_4$, the maximum amplitude of oscillation was 10.5 mA. According to literature, the first dissociation constant, K of H$_3$PO$_4$ is 7.6 $\times$ 10$^{-3}$. The H$_3$PO$_4$ concentration range of 0.4–1.1 mol·L$^{-1}$ correspond to the pH value range of 1.29–1.06 for the bulk solution, and it is present as A lot of H$_2$PO$_4^-$, H$_3$PO$_4$ and a small amount of H$_4$PO$_4^{+}$ in the phosphoric acid solution. When H$_3$PO$_4$ concentration increased to 1.2 mol·L$^{-1}$, the pH of the
corresponding bulk solution decreased and the \( \text{H}_3\text{PO}_4^+ \) increased in the solution. At the same time, the EOs disappeared, which indicate that \( \text{H}_3\text{PO}_4^+ \) was not conducive to the formation of oscillation. According to the experimental results, for oscillation to occur, sufficient levels of \( \text{H}_2\text{PO}_4^- \) must be present. This conclusion indirectly verified that the deposited surface of the electrode was \( \text{CuH}_2\text{PO}_4 \).

Figure 6a presents the effect of different \( \text{CuSO}_4 \) concentrations on CV with 1.0 mol·L\(^{-1}\) \( \text{H}_3\text{PO}_4 \). EOs are detectable when the \( \text{CuSO}_4 \) concentration is in the range of 0–3.2 m mol·L\(^{-1}\). With the increase of \( \text{CuSO}_4 \) concentration to 4, or even 8 mmol·L\(^{-1}\), EOs disappeared. Figure 6b presents the effect of different \( \text{CuSO}_4 \) concentrations on the potential range and the maximum amplitude with 1.0 mol·L\(^{-1}\) \( \text{H}_3\text{PO}_4 \). In Fig. 6b, both voltage range and maximum amplitude value of EOs initially ascended and then declined with increasing \( \text{CuSO}_4 \) concentration. At 2.4 m mol·L\(^{-1}\) \( \text{CuSO}_4 \), the oscillating voltage range was as high as 0.44 V, and the maximum amplitude value was 13 mA. At low \( \text{CuSO}_4 \) concentrations, \( \text{Cu}^{2+} \) reacts with \( \text{Cu} \) to form \( \text{Cu}^{2+} \),\(^{27} \) accelerating the occurrence of EOs. In combination with the experimental results by Aksu, \( \text{Cu}^{2+} \) reacted with \( \text{H}_2\text{PO}_4^- \) to produce \( \text{Cu(H}_2\text{PO}_4)_2 \), and the reaction constant \( k \) was 10\[^{0.22\text{,}26} \). Hence, \( \text{Cu}^{2+} \) easily combines with \( \text{H}_2\text{PO}_4^- \) to form \( \text{Cu(H}_2\text{PO}_4)_2 \) at high \( \text{CuSO}_4 \) concentrations, leading to the disappearance of the oscillation.

### 3.4 Effect of stirring rate on EOs

The effects of stirring rate on EOs were investigated. As shown in Fig. 7, EOs occurred within the potential range of 1.71–1.93 V without stirring. The oscillation was pushed back and was found within 1.80–1.97 V when the electrolyte was subjected to magnetic stirring at 400 rpm. When the stirring rate was increased to 800 and 1200 rpm, the oscillation was pushed back and occurred within 1.92–2.05 and 2.04–2.14 V, respectively, clearly destroying the regularity. Furthermore, the regularity of EOs disappeared when the stirring rate was increased to 1600 rpm or higher. Under 0–1200 rpm stirring, the oscillation still existed but the range at which it was generated changed. This finding indicated that liquid phase mass transfer and electron transfer steps mainly affected the oscillation. The analysis shows that stirring can effectively reduce concentration polarization. EOs mainly caused by liquid phase mass transfer weaken or even disappear. At the same time, accelerating the stirring rate, which attenuated the coupling effect between the liquid phase mass transfer and the electron transfer step, destroyed the turbulent nature of fluid flow and weakened the oscillation. At high-speed stirring, a vortex center formed in the center of the electrolyte, seriously hindering the electrode reaction and leading to the disappearance of the oscillation.

3.5 Effect of temperature on EOs

The effect of temperature on EOs were studied by gradually increasing the temperature from 12 to 40°C. As shown in Fig. 8, at 12°C, oscillations occurred within 1.70–2.00 V, and the corresponding signal was relatively obvious. As the temperature increased to 30°C, the oscillation signal significantly attenuated within 1.86–2.00 V. At temperatures above 34°C, the oscillation signal either weakened or even disappeared. At the same time, the temperature above 34°C did not produce any substance on the copper anode surfaced similar to the brown substance in the cd section of Fig. 1a, therefore, the EO phenomenon did not occur. Hence, the effect of temperature on EOs is significant. This result is attributed to the effect of temperature on both liquid phase mass transfer and electron transfer steps. Hence, the temperature should be controlled within the range of 12–30°C to occur EO phenomenon and to better understand the oscillation mechanisms.

3.6 Effect of scanning speed on CV

The red line was acquired from low to high anodic potentials, and the black line was obtained from high to low anodic potentials.
Comparison of Figs. 1 and 3 showed that the oscillation ranges differed between CV and I–t curves because the reaction time was differed during testing. CV curves were obtained on fresh copper electrodes using different scanning speeds and compared to determine the effect of reaction time of the electrode on oscillations. During the experiment, scanning speeds of 1, 5, 10, 50, 100, and 500 mV·s\(^{−1}\) were used within the scanning potential range of 1.55–2.40 V. As shown in Fig. 9a, oscillation does not occur when the scanning speed was 1 mV·s\(^{−1}\). When the scanning speed was increased to 5 mV·s\(^{−1}\), oscillation appeared but was not continuous within the range of 1.78–1.92 V during oxidation on the Cu electrode (red line in Fig. 9b). When the scanning speed was increased to 10 mV·s\(^{−1}\), the oscillation was continuous and evident within 1.78–1.95 V (red line in Fig. 9c). Moreover, oscillation was rapidly formed and gradually disappeared. When the scanning speed increased to 50 and 100 mV·s\(^{−1}\), oscillation occurred within 1.63–2.06 V (red line in Fig. 9d) and 1.74–2.00 V (red line in Fig. 9e), respectively, their frequencies were smaller than that of 10 mV·s\(^{−1}\). EOs disappeared when scanning speed was raised to 500 mV·s\(^{−1}\). The effect of scanning speed on oscillation was remarkably evident. The scanning speed was extremely rapid enough not to detect the oscillation signal, because the film formation rate on the electrode surface did not quite match the sensitivity of the test or the receiver instrument of the electrochemical workstation. When the scanning speed exceeded 5 mV·s\(^{−1}\), the significant EO signal was detectable. Under low scanning speeds, complex electrochemical reactions occurred in the electrode, leading to delayed signals of the electrode reaction. Therefore, a scanning speed of 10 mV·s\(^{−1}\) was used in subsequent experiments.

### 3.7 Electrode reaction mechanism of EOs

Similar redox reactions were reported in the studies on the reaction between Cu\(^{+}\) and H\(_3\)PO\(_4\). Oxidization produces the following potential intermediates: Cu\(^{2+}\), Cu\(^{+}\), CuH\(_2\)PO\(_4\), H\(_3\)PO\(_4\), H\(_2\)PO\(_4\)\(^−\), and H\(^+\),\(^{26,28}\) which react with one other to finally produce Cu\(^{+}\). According to the theory of Prigogine,\(^{29}\) the effect of the deposition and dissolution of CuH\(_2\)PO\(_4\) may provide essential nonlinear items for the mechanism of EOs through electro-oxidation of the Cu anode. The possible reactions are summarized as follows:\(^{30−32}\)

\[
\begin{align*}
    \text{Cu} & \xrightarrow{k_1} \text{Cu}^{+} + e^- \\
    \text{H}_3\text{PO}_4 & \xrightarrow{k_2} \text{H}^+ + \text{H}_2\text{PO}_4^- \\
    \text{Cu}^+ + \text{H}_2\text{PO}_4^- & \xrightarrow{k_{1-2}} \text{CuH}_2\text{PO}_4 \\
    \text{CuH}_2\text{PO}_4 + \text{H}^+ & \xrightarrow{k_3} \text{Cu}^{2+} + \text{H}_2\text{PO}_4^- + e^- \\
    \text{Cu}^+ & \xrightarrow{k_4} \text{Cu}^{2+} + e^- \\
    \text{Cu}^+ & \xrightarrow{D_1} \text{Cu}^{+} (\text{bulk}) \\
    \text{Cu}^{2+} & \xrightarrow{D_2} \text{Cu}^{2+} (\text{bulk})
\end{align*}
\]

where Cu is the reaction surface without a film of CuH\(_2\)PO\(_4\) salt; Cu\(^{+}\) and Cu\(^{2+}\) represent cuprous and cupric ions adjacent to the electrode surface, respectively; CuH\(_2\)PO\(_4\) is the electrode surface with a film covering the Cu anode surface; \(k_1, k_2, k_3, k_4,\) and \(k_5\) are rate constants;\(^{33}\) and \(D_1\) and \(D_2\) is the diffusion coefficient that includes the effect of the thickness of the diffusion part.
During the dissolution of the Cu anode, the concentrations of Cu$^{2+}$ and Cu$^{+}$ adjacent to the electrode surface may change because of electrode dissolution. Consequently, the diffusion potential in the double layer changed with increasing Cu$^{2+}$ and Cu$^{+}$ concentration, thereby influencing the reaction rate of electrode dissolution. This coupling may result in a full dynamic behavior.\(^{34,35}\)

First, as shown in Fig. 4, EO frequency linearly increased with potential. The frequency of oscil- lation directly increased with increasing potential. The frequency of oscillation increased with increasing temperature, indicating that the equilibrium constants and the rate constants are consistent with the van’t Hoff form.\(^{35}\)

The mechanism of periodic EOs in Cu electro-oxidation of phosphoric acid solution was fully systematic studied through experiment and theoretical analysis. Moreover, the stirring rate is associated with the diffusion coefficient $D_1$ and $D_2$. This finding indicated that liquid phase mass transfer and electron transfer steps mainly affect EO. Hence, the results of this simplified model are consistent with the experimental results. EOs occurred as a result of CuH$_2$PO$_4$ deposition and dissolution through electro-oxidation of the Cu anode. This study provides insights into the relevance between the micro-chemical mechanisms for the macroscopic non-equilibrium phenomenon and presents novel concepts for developing highly efficient electrode dissolution in metallurgy.

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