Int. J. Electrochem. Sci., 15 **(2020)** 9532 – 9542, doi: 10.20964/2020.09.85

International Journal of
ELECTROCHEMICAL
SCIENCE
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Characteristic and Control of Electrochemical Oscillation at the Anode during Electrolytic Refining Copper

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Received: 4 June 2020 / *Accepted:* 20 July 2020 / *Published:* 10 August 2020

Electrolytic refining copper production is a high-energy hydrometallurgical industry. The key to develop a new method for energy-saving electrolysis of high-purity cathode copper is to reduce the electrical-energy consumption of electrochemical oscillations (EOs) at the anode. This phenomenon cannot be explained based on traditional equilibrium thermodynamics theory. In this paper, a simplified electrolytic copper system was used with H_2SO_4–$CuSO_4$ solution to research the behaviour and characteristic of EOs at the anode, as well as to analyse the mechanism of EOs and the effect of potential on EOs.The electrochemical oscillation was regulated by improving the anode (such as copper anode and lead dioxide anode) and introducing additives (such as hydrochloric acid, thiourea and bone glue). The obvious inhibition effect of thiourea and lead dioxide anode on electrochemical oscillation was found, so as to improve the electrolysis process. It is possible to find a new energy-saving and environmental protection electrolysis working area in the equilibrium zone.

Keywords: Electrochemical oscillation, Electrolytic refining, Copper anode, Electrodissolution, Energy-saving

1. INTRODUCTION

The industry of electrolytic copper consumes large amounts of resource and energy and causes heavy pollution. Reducing the power consumption of high-purity cathode copper produced by electrolysis has become a research hotspot. The first type of method is the improvement of electric-field factors, such as power supply and plate structure, and the regulation of the electric field by periodic reverse-current method [1], pulse-current method, and stainless-steel cathodic electrolysis method [2]. The second type of method involves studying chemical factors such as electrolytes and additives. Some commonly used additives include gelatin, thiourea, casein, and chloride [3]. The third type of method includes the influence of electrolyte flow factors and the movement of bubbles such as hydrogen, as well as the temperature distribution of the electrolytic cell. For example, using ultrasonic in copper electrolytic refining is beneficial for eliminating concentration polarisation and increasing current density[4]. In summary, the traditional research is based on the effects of electric field, chemical field, flow field, temperature field and other factors on the macroscopic effect of electrolysis; however, the micro action mechanisms of the electrode reaction and copper deposition have not been explored, thereby hindering power-consumption reduction and product improvement[5].

In the production process, on the anode copper is dissolved in the form of Cu^+, in addition to Cu^{2+}. In the traditional research it often analyse the electrolytic copper process from the perspective of equilibrium thermodynamics. its electrolysis mechanism is simplified, so it exist some differences with the experimental observations. In fact, in the industrial electrolysis process, generally high concentrations, large currents, fluidity and other characteristics are observed that are far from the reaction equilibrium[6,7]. Electrochemical systems often have some elementary-reaction steps of EOs. As the system moves away from equilibrium under the electric field, the influence of the term of EOs is more significant, and even spatiotemporal ordered phenomenon, such as EOs occurs[8]. EOs have long been discovered in actual electrolytic copper. Potkonjak et al. [9] found complex EOs behaviour in copper electrolysis with trifluoroacetic acid. And the experimental results show that the oscillation of the applied potential is actually the oscillation of the double-layer potential. At constant current, Hai et al. found that there was a negative differential resistance in the system, which led to potential oscillation[10], and studied the inhibitory effect of the copolymer of imidazole and 1,4-butanediol diglycidyl ether on the oscillation [11]. Ding et al. [12] found significant current oscillations during the electrolysis of potassium permanganate and established the energy-consumption formula of the current oscillation in the system. In the electrolysis of potassium permanganate, the energy consumption caused by the current oscillation behaviour is high to 30.0%; hence, the electrolysis energy caused by EOs cannot be ignored.

Current research found that the voltage of the electrolytic copper process deviates far from the equilibrium voltage and the nonlinear mechanism exists in the redox reaction, leading to the occurrence of spatiotemporal-ordered phenomenon, such as EOs. Many scholars have further explored the initial mechanism of EOs in the electrolysis process, which can be divided into three categories. First, the electrode surface material periodically precipitates and dissolves to form an oscillation. Potkonjak et al.[13] found current oscillation during the dissolution of anodic copper in trifluoroacetic acid solution, which is considered to be caused by the periodic formation and dissolution of the white film on the surface of copper electrode. Glarum et al.[14] found oscillations in the Cu/H_3PO4 system, resulting from the deposition and dissolution of the film of anodic copper surface. Kamiya et al.[15] found that the copper thiocyanate formed adsorb onto on the surface of copper electrode by the combination of copper ions and thiocyanate ions, and it would occur precipitation–dissolution to cause self-generated oscillation. Barkey et al.[16] found a voltage oscillation phenomenon on a rotating disk electrode or a ring-disk electrode during constant-current copper electrolysis in sulphuric acid containing additives , and found that the electrochemical oscillation was the result of coupling dynamic variable overpotential and additional surface coverage of the cathode. The oscillation is caused by the periodic variation of the intermediate state ionic at the electrode interface. Schaltin et al.[17] found current oscillations in the interconversion process of Cu^{2+} and Cu^{+} in a copper-containing imidazole ionic liquid. Eskhult et al.[18] found current oscillations caused by the alternating synthesis of Cu and Cu_2O nanolayer materials in alkaline $Cu(II)^{-}$ citric acid solution. Finally, the periodic generation of bubbles on the electrode surface slows down the electron exchange reactions, which resulting in oscillation. Mukouyama et al. [19] found EOs behaviour in the hydrogen evolution reaction in the electrolytic water, which can occur in different kinds of acids and on the surface of metals. Thus, the mechanism of oscillation can be explained by the autocatalysis of the bubble at the electrode interface.

Research on EOs in electrolysis process is currently limited to the discovery of its phenomena and the speculations of its preliminary qualitative mechanism. Studies on the types and quantitative mechanisms of EOs in different electrolysis systems are few[20,21], which greatly restricts investigation of phenomenon and mechanism of EOs in electrolytic copper process. In this paper, it aimed to use the system consistent with the actual electrolytic refining copper industry to explore the dynamics and characteristics of EOs in the electrolysis. By studying the dynamics mechanism of EOs in the system and changing the electrolyte composition and the externally controlled electrolysis conditions of EOs, a theory for a new energy-saving way of constructing electrolytic copper was provided.

2. EXPERIMENT

All reagents were analytical grade. Unless specifically noted, the fresh electrolyte B_0 contained 2.05 $mol \cdot L^{-1}$ H_2SO_4 (98%, Tianjin Yaohua Chemical Reagent Co.) and 0.7 $mol \cdot L^{-1}$ $CuSO_4$ ($\geqslant$99.0%, Tianjin Zhiyuan Chemical Reagent Co.), and the scanning speed of the cyclic voltammetry was 50 $mV \cdot s^{-1}$. Water was purified using a water purification system (PALL Cascada II I 30, USA).

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, unless specially noted, the counter electrode was a 304 stainless steel sheet (3 cm × 3 cm); and the work electrode was a copper plate (1 cm × 1 cm, 99.95% purity). Except for the effective area of the work electrode, the remaining areas were sealed with an insulating polymer to prevent fluctuation in the area during testing. The distance between the work electrode and the counter electrode was 7.0 cm. All electrodes were finely polished and cleaned in acetone and purified water [22,23]. Electrolytic cell was placed in a heat collector-constant temperature-type magnetic stirrer (DF-101S, Shanghai, China) to maintain the electrolyte at 335 K.

Additives were included in the above electrolyte B_0 to study the effect of the additives on EOs. Referring to the additives and their concentrations commonly used in the industry, the additives used in the experiment were hydrochloric acid (HCl, 0.6 mL/L), thiourea (TA, 3.0 mg/L) and bone glue (BG, 2.4 mg/L). Three sets of electrode pairs were used in the above electrolysis system to investigate the effect of the electrode materials on EOs. In the first group, an anode copper electrode (1 cm × 1 cm) was used as a working electrode, and a platinum plate (3 cm × 3 cm) was used as a counter electrode. In the second group, in order to simulate industrial production, an copper electrode (1 cm × 1 cm) was used as a working electrode, and a 304 stainless steel (3 cm × 3 cm) was used as a counter electrode. In the third group, a novel lead dioxide electrode (1 cm × 1 cm) was used as a working electrode, and a 304 stainless steel (3 cm × 3 cm) was used as a counter electrode. In the above three sets of electrodes, the reference electrodes all were saturated calomel electrodes (SCE).

The scanning speed of the cyclic voltammetry (CV) was 50 $mV\cdot s^{-1}$, and that of the current - time curve (I-t) was 0.1 s^{-1}. HITACHI SU8010, field emission environmental scanning electron microscope and energy dispersive spectrometer (SEM-EDS) was used for surface investigation and feature detection. Images and spectra were collected at 20 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI-5400 spectrometer.

3. RESULTS AND DISCUSSION

3.1 Current oscillations on the Cu anode

The CV experiment used a three-electrode system, the working electrode was a copper electrode, the reference electrode was SCE, and the counter electrode was stainless steel. At 335K, significant EOs were observed in 2.05 $mol\cdot L^{-1}$ concentrated sulphuric acid and 0.7 $mol\cdot L^{-1}$ copper sulphate solution without stirring.

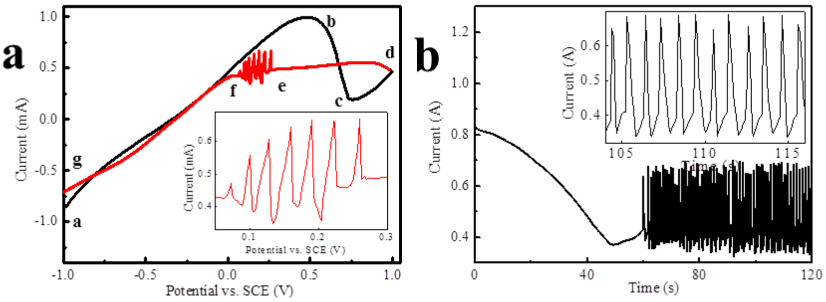

Figure 1. (a) CV of the Cu anode in 2.05 $mol\cdot L^{-1}$ H_2SO_4 and 7.00 $mol\cdot L^{-1}$ $CuSO_4$ (inset is the partially enlarged image). (b) I-t curve under constant potential of 0.20 $V_{vs\ SEC}$ electrolysis (inset is the partially enlarged image).

Fig. 1a shows the CV curve measured over a voltage range of −1.0 V to 1.0 $V_{vs\ SEC}$. The ad segment black line indicates the anode forward scan curve and the dg segment red line indicates the anode reverse scan curve. No oscillation was observed in the ad segment. The peak at b point is an oxidation peak. The experiment shows that in the ab segment, increased current lead to an obvious bright and dissolution phenomenon on the copper-sheet surface. The current value of the bc segment was significantly reduced, and a brownish red film formed on the copper surface. The cd segment current value increased slightly, and the material on the copper surface slightly fell off. The de segment current changed a little, and the brown-red material on the electrode surface hardly changes. In the e point EOs occurred, and that disappears when it reached point f. The brownish red material fell off on the surface of electrode in the ef segment slightly. The brownish red film quickly fell off on the copper surface in the fg segment. During the reaction of the dg segment, copper ions in the solution were continuously deposited on the counter electrode, and platinum surface was covered with a purplish red substance. Fig. 1b is a partial enlarged view of the ef segment in the CV curve showing that the oscillation phenomenon occurred at 0.05 $V_{vs\ SEC}$ to 0.27 $V_{vs\ SEC}$.

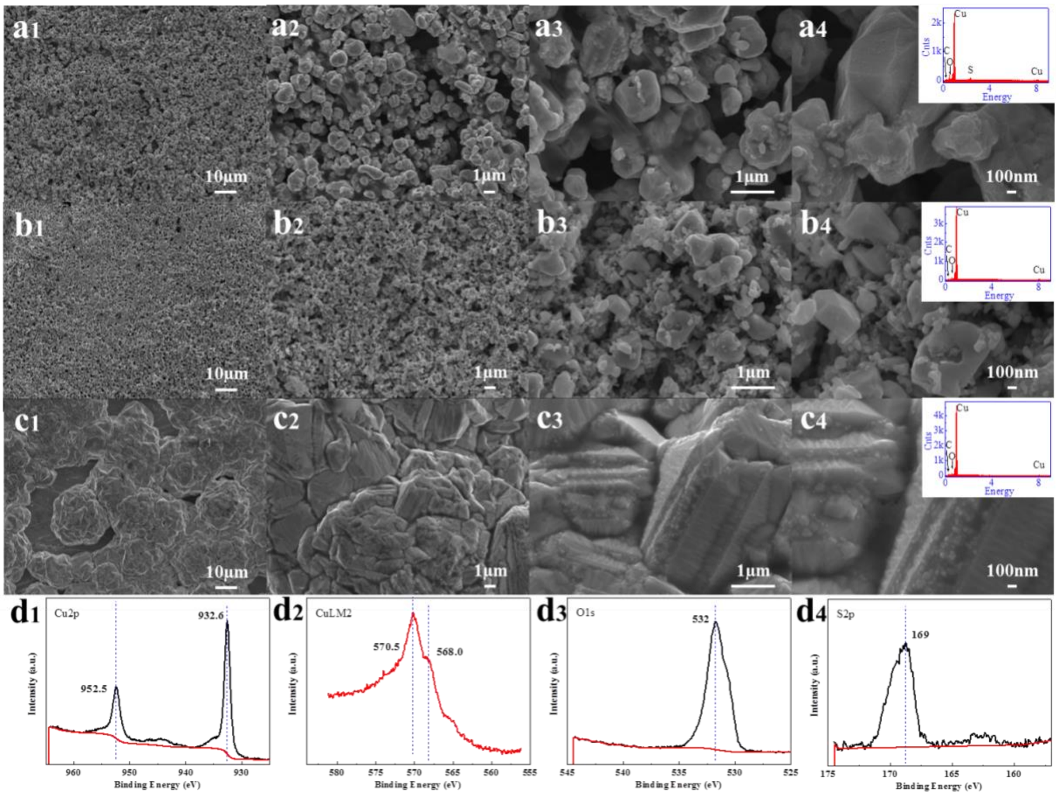

Figure 2. Different magnification times of SEM-EDS surface layer formed on the electrode surface when the current–time curve was under constant potential, (a) Substance on the WE at 0.20 $V_{vs\ SEC}$, (b) Substance on the WE at 0.35 $V_{vs\ SEC}$, and (c) Substance on the CE at 0.20 $V_{vs\ SEC}$, (d) XPS of the substance on the WE at 0.20 $V_{vs\ SEC}$

Fig. 1b shows I-t curve at constant voltage of 0.20 $V_{vs\ SEC}$, and the inset shows the regular periodic oscillations. The I–t curve was obtained for 120 s at 0.20 $V_{vs\ SEC}$. Fig. 1b inset selects the oscillation in the period of 105–115 s and enlarges it locally to obtain the conclusion that regular current oscillation can occur in the acidic system. When EOs occurred, WE and CE electrodes were taken out and dried for SEM-EDS analysis as shown in Figs. 2a and 2c. XPS analyses are shown in Fig. 2d. At the same time, after testing the I–t curve for 120 s at 0.35 $V_{vs\ SEC}$, EOs was not observed. The WE electrodes were taken out and dried for SEM and EDS analyses, as shown in Fig. 2b. Before testing, the electrodes were cleaned in six beakers containing deionized water. Finally, the electrodes were dried and wrapped in fresh-keeping film.

Combined with the results of SEM-EDS analysis, C is mainly the conductive adhesive used for the test, and the element is not introduced into the solution; hence, it can be ignored. As shown in Fig. 2a, when oscillation occurs at 0.20 $V_{vs\ SEC}$, the surface of WE was covered with a layer of material with obvious pore structure, mainly composed of particles of different sizes of 0.1−1.0 μm. This material contains Cu, S and O. As shown in Fig. 2b, when no oscillation occurs at 0.35 $V_{vs\ SEC}$, a relatively dense material appears on the WE surface relative to oscillation and is mainly composed of particles of different sizes ranging from 0.1–0.6 μm. This material contains only Cu and O. Therefore, compared with that with oscillation, the surface film of WE was finer and denser when no oscillation occurred. This result may be due to the fact that when oscillation occurred, the film was relatively porous and the copper sulphate electrolyte was more likely to penetrate. As shown in Fig. 2c, when oscillation occurred at 0.20 $V_{vs\ SEC}$, the material on the CE surface was mainly composed of 15–20 μm clusters, and the crystal nucleus was mainly composed of 2–5 μm irregular particles. This material contained a large amount of Cu and a very small amount of O, consistent with the results observed in the purple material (Fig. 1a).

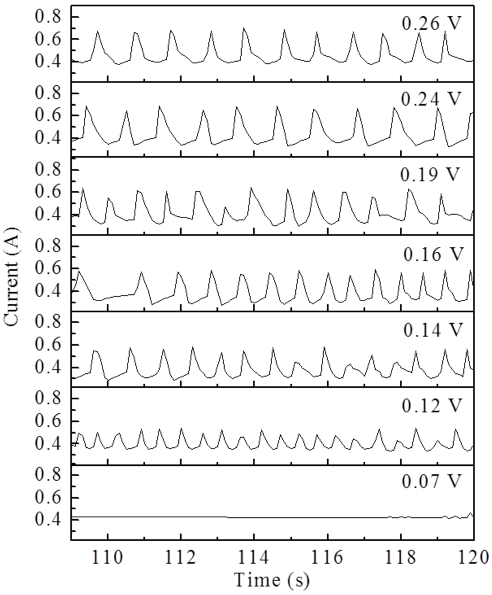

Figure 3. I–t curves at different potentials in H_2SO_4–$CuSO_4$ solution.

Two predominant peaks (Fig. 3d) at 932.6 and 952.5 eV complied with the Cu 2p 3/2 and Cu 2p 1/2 of Cu_2O, respectively [24,25]. The Cu LM2 auger spectra confirmed the presence of Cu^0 at a binding energy of 568.0 eV[26]. The S 2p peak observed at 169 eV is attributed to surface sulphur with high oxide state, such as sulphates[27]. The peaks at 932.6, 169, and 532 eV of the spectra shown in Fig. 2d were attributed to the $CuSO_4$ species. Combining the test results of XPS and EDS, the deposited materials are CuSO4 and Cu2O on the electrode surface. Hence, this conclusion is consistent with the previous EDS results.

3.2. Effect of potential on EOs

In the above systems, I-t curves were obtained using the same fresh electrode under different potential. Fig. 3 summarises the 109–120 s for the I–t curves detected from 0.07 $V_{vs\ SEC}$ to 0.26 $V_{vs\ SEC}$.

The oscillation was first fixed at a constant potential of 0.05 $V_{vs\ SEC}$, resulting in the I–t curve, which approached a straight line. With further increased potential to 0.07 $V_{vs\ SEC}$, almost no oscillation occurred at the beginning, and a very weak oscillation signal was observed starting between 118–120 s. EOs gradually improved from 0.12 $V_{vs\ SEC}$ to 0.24 $V_{vs\ SEC}$, and oscillations gradually weakened from 0.24 $V_{vs\ SEC}$ to 0.26 $V_{vs\ SEC}$. With further increased voltage, EOs disappeared. EOs emerged from 0.05 Vvs SEC and disappeared at 0.27 Vvs SEC in CV of Fig. 1. EOs ranges of Figs. 1 and Figs. 3 were slightly different. With using the same electrode and increasing gradually in applied potential, the test time for CV was shorter than that for I-t at the same potential.

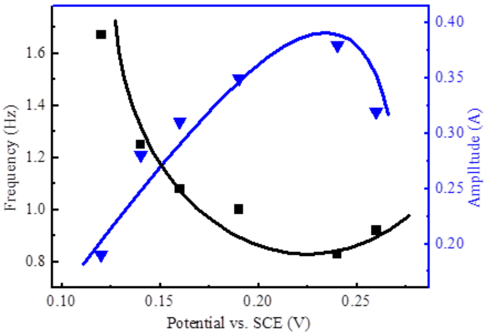

Figure 4. Dependence of amplitude and frequency on different potentials.

Moreover, the effect of potential on amplitude and frequency was shown in Fig. 4. When the electrochemical systems were same and the stable current EOs were generated, the frequency of EOs was decreased with increased potential. With increased potential, the amplitude of EOs first increased and then gradually decreased. In Figs.1 and 3, they both indicated that EOs increased with increased potential, which illustrated that the result from Fig. 4 were consistent with that from Fig. 1. In addition, this result is consistent with the change rule of copper electrode in pure phosphoric acid and pure hydrochloric acid system [28, 29]. Therefore, the influence of voltage on electrochemical oscillation is consistent.

3.3. Effect of electrolyte composition on EOs

The effect of each component in the solution on the oscillation was investigated. As shown in Fig. 5a, the CV curves of four solutions of B_0, B_0+HCl, B_0+HCl+TA and B_0+HCl+TA+BG were scanned under the conditions of fresh electrode, constant temperature of 335K, no stirring, stainless steel as the counter electrode and copper as the working electrode. Figs. 5b and 5c show The effect of voltage on frequency and amplitude of oscillation between 0–120 s in the potential range of 0.03–0.35 $V_{vs\ SEC}$ in the I-t curve in the above four solutions. Fig. 5a shows that regular oscillations occur in the range of 0.03–0.35$V_{vs\ SEC}$. For B_0 only solutions, the periodic oscillation voltage range was 0.04–0.18 $V_{vs\ SEC}$. With increased voltage, the frequency initially increased and then decreased (Fig. 5b). At a voltage of 0.10 $V_{vs\ SEC}$, the frequency reached up to 1.17 Hz. With increased voltage, the amplitude increased (Fig. 5c).

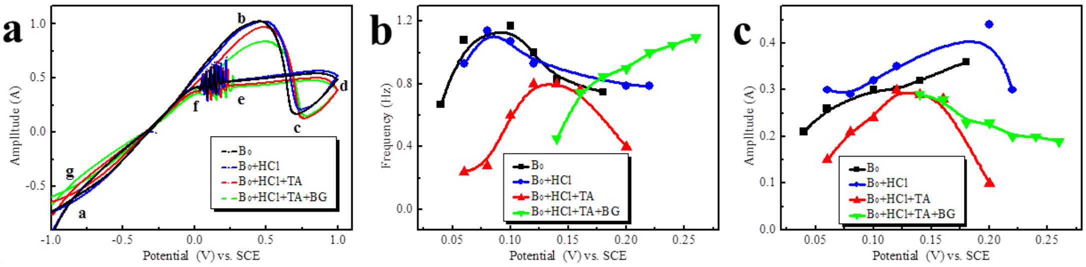

Figure 5. Effect of different electrolyte composition on EOs, (a) CV; (b) Dependence of frequency on potentials; (c) Dependence of amplitude on potentials

At a voltage of 0.18 V versus SCE, the amplitude reached up to 0.36 A. After adding HCl to the B_0 solution, the voltage range of the periodic oscillation was 0.06–0.22 $V_{vs\ SEC}$. The voltage range of the oscillation in CV curve is expanded. The frequency initially increased and then decreased gradually with increased voltage. At a voltage of 0.08 $V_{vs\ SEC}$, the frequency reached up to 1.14 Hz. With increased voltage, the amplitude increased gradually and then decreased. At a voltage of 0.20 $V_{vs\ SEC}$, the amplitude reached up to 0.44 A. Comparing the system of B_0 and B_0+HCl, the oscillation curves of the two systems were similar, which shows that the effect of HCl on the oscillation was small. After TA was added to the B_0+HCl solution, the period of the periodic oscillation was in the range of 0.06–0.20 $V_{vs\ SEC}$. The effect of voltage on frequency and amplitude of oscillation rapidly increased and then decreased. At a voltage of 0.12 $V_{vs\ SEC}$, the maximum frequency was only 0.8 Hz, and the maximum amplitude was only 0.29 A. However, compared with the system of B_0 and B_0+HCl, the amplitude and frequency of the oscillation in the system of B_0+HCl+TA were significantly smaller at the same voltage. Therefore, after adding TA to the electrolyte, the oscillation could be obviously suppressed. In the system of B_0+HCl+TA+BG, the voltage range of the periodic oscillation was 0.14–0.26 $V_{vs\ SEC}$. With increased voltage, the frequency of oscillations increased rapidly and the amplitude of oscillations decreased gradually. At a voltage of 0.26 $V_{vs\ SEC}$, the maximum frequency was 1.10 Hz; and at a voltage of 0.14$V_{vs\ SEC}$, the maximum amplitude was 0.29 A. Therefore, adding BG in the electrolyte has a significant effect on the oscillation. Finally, the experiment concluded that the potential range of the periodic oscillation gradually shifted to a large voltage range after the HCl, TA and BG additives were sequentially added to the B_0 solution. The HCl addition exhibited little effect on the EOs phenomenon. The TA addition significantly inhibited the EOs phenomenon, whereas the BG addition strengthened the EOs phenomenon. After adding hydrochloric acid, it is believed that Cl^- will activate the electrode and depolarize the anode. In addition, Cl^- will form a complex with dissolved copper ions and adhere to the surface of the copper anode, which promotes the formation of CuO and Cu_2O to a certain extent, so the addition of hydrochloric acid has little effect on the electrochemical oscillation. After adding thiourea, thiourea can depolarize the anodic dissolution, and the cumulative depolarization of thiourea and hydrochloric acid increases. In addition, thiourea and copper ions will form complex and adsorb on the surface of the anodic the cathode. Therefore, the migration of divalent copper ions from anode to solution and reduction on cathode are hindered, which is not conducive to the dissolution and deposition of Cu_2O. When bone glue was added, the viscosity of electrolyte increased, and the polarization of electrodes increased. When bone glue was added, thiourea was adsorbed on the surface of colloidal particles, which reduced the effective quality of thiourea and inhibited the effect of thiourea to a certain extent.

3.4. Effect of different electrode materials on EOs

In order to study the effect of different electrode materials on the oscillation, fresh electrodes were used for each test, and the CV curve was measured with the same solution and different combinations of electrodes. Fig. 6a shows the CV curve obtained when only copper sulphate and sulphuric acid were used in the solution and when copper was used as a working electrode. Among them, the black line was obtained by using platinum as the counter electrode, the blue line was obtained by using stainless steel as the counter electrode, and the peak of the oxidation peak was almost unchanged when platinum or stainless steel was used as the counter electrode.

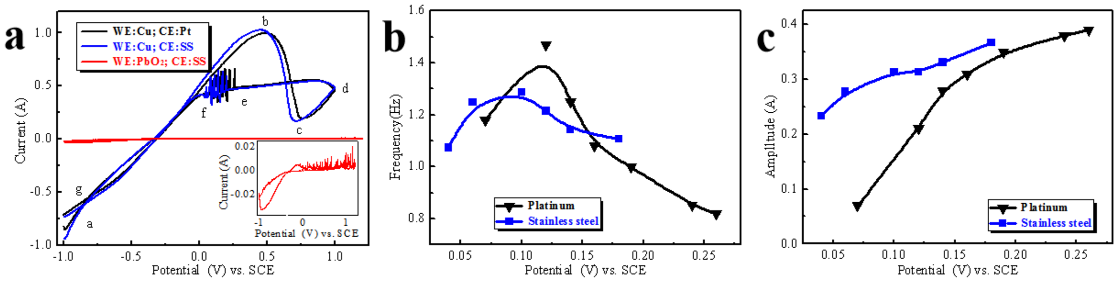

Figure 6. Effect of different electrode materials on EOs, (a) CV; (b) Dependence of frequency on potentials; (c) Dependence of amplitude on potentials; (a inset): enlarged image of the CV curve of stainless steel as the counter electrode, and lead dioxide as the working electrode

However, when the platinum sheet was used as the counter electrode, the peak potential of the oxidation peak increased and the potential range in which the oscillation started and disappeared also increased, shifting to the large potential. The red curve was the CV curve obtained with lead dioxide as the working electrode and stainless steel as the counter electrode. After using lead dioxide as the working electrode, the anodized peak disappeared and the periodic oscillation was obviously destroyed. However, after amplification, many irregular weak oscillation signals were observed (Fig. 6a inset), the oscillation range widened, and the amplitude of the oscillation weakened and even became negligible. The effect of lead dioxide electrode on suppressing oscillation was extremely obvious. Figs. 6b and 6c show the effect of voltage on frequency and amplitude of oscillation between 0–120 s of I-t curve. When a platinum electrode or a stainless-steel electrode was used as the counter electrode, the frequency initially increased and then decreased with increased voltage, but the amplitude consistently increased. Moreover, the variation rules of the two-electrode systems were the same, and the data change values were almost the same. Therefore, the working electrode material greatly influenced the oscillation.It may be due to the different deposition potential of copper on platinum sheet and stainless steel sheet, which results in different mechanical behavior. In traditional electrolytic copper refining process, coarse copper is anode and the anode copper dissolves obviously with the progress of electrolytic refining process, Therefore, insoluble anode lead dioxide is used for electrolysis and it is found that lead dioxide as anode can significantly inhibit the electrochemical oscillation..It is said that lead dioxide is used as an anode, the dissolution process of copper anode will not occur, and the surface of the anode will not be enriched with Cu^{2+}, inhibiting deposition-dissolution of Cu_2O. Under experimental conditions, a large number of bubbles on the surface of the lead dioxide electrode will emerge, forming air resistance to a certain extent. As bubbles continue to form, it can cause slight electrochemical oscillation.

Table 1. Effects of main salts on the EDS of the surface layer

Sample	Cu(wt%)	C (wt%)	O (wt%)	S (wt%)
a	90.68	1.45	4.88	2.99
b	98.16	0.85	1.00	0
c	97.39	1.60	1.01	0

4. CONCLUSIONS

Regular periodic EOs phenomenon occurred in the CV curve for the fresh copper electrode in 2.05 $mol\cdot L^{-1}$ H_2SO_4 and 7.00 $mol\cdot L^{-1}$ $CuSO_4$ solution at 335K without mixing. Regular periodic oscillations occurred at 0.05–0.27 $V_{vs\ SEC}$ in the CV curve, and the I-t curve also indicates oscillation at 0.07–0.26 $V_{vs\ SEC}$. When oscillation occurs, a substance with a pore structure composed of particles of different sizes ranging from 0.1 μm to 1.0 μm appeared on the surface of the WE. The material was mainly $CuSO_4$ and brown-red Cu_2O as indicated by EDS and XPS results. When the oscillation disappears, the material on the electrode surface was mainly composed of brown-red Cu_2O particles of different sizes ranging from 0.1 μm to 0.6 μm. When the main film was loosely porous, the H_2SO_4–$CuSO_4$ electrolyte easily penetrates into the electrode surface. Thus, electro-oxidation of the fresh Cu anode caused periodic deposition and dissolution of the Cu_2O particles on the electrode surface, which causes periodic current oscillation.

The effects of additives and electrode materials on the vibration in the electrolyte were further analysed. Adding HCl to the above B_0 solution has little effect on EOs, adding TA significantly inhibits the EOs phenomenon, and adding BG enhances the EOs phenomenon.

After changing the Cu electrode to the PbO_2 electrode, the vibration phenomenon was significantly reduced or even negligible.

By adding hydrochloric acid, thiourea and changing working electrode, it was found that adding hydrochloric acid, thiourea or lead dioxide as anode had obvious inhibition effect on electrochemical oscillation,and lead dioxide as anode has the most obvious inhibiting effect on the electrochemical oscillation, which provided a new idea for reducing power consumption caused by electrochemical oscillation.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation of China (NSFC51604180), Cultivate Scientific Research Excellence Programs of Higher Education Institutions in Shanxi (CSREP2019KJ038), General Project of Shanxi Province Key R & D Plan (Social Development Field, 201903D321068), the Applied Basic Research Programs of Science and Technology Department of

Shanxi Province (201701D221036), Scientific and Technologial Innovation Programs of Higher Education Institutions in Shanxi (2019L0235).

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