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# Copper corrosion and anodic electrodisolution mechanisms in naturally aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub>

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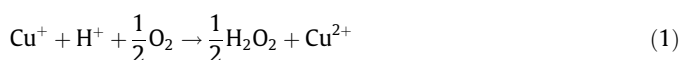
## ABSTRACT

Mechanisms of copper corrosion and electrodisolution in naturally aerated, stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> were investigated by means of electrochemical techniques, compared with deaerated measurements. The role of dissolved oxygen was suggested, and three models were proposed in −0.05 ~ 0.15 V vs. SCE range. Near to corrosion potential, chemical redox between cuprous intermediate and oxygen reduction reaction (ORR) intermediate accelerated copper corrosion, and corrosion rate was controlled by a combined cathodic kinetic–anodic diffusion process. In low and high potential ranges, chemical redox, occurred between cuprous intermediate and oxygen molecule, synergistically accelerated the electrodisolution of copper.

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## 1. Introduction

Anodic dissolution of copper in H<sub>2</sub>SO<sub>4</sub> is frequently studied in many areas, such as in electrodisolution processes (including electrorefining, electropolishing, electromachining, etc.) [1–7], corrosion and inhibition [8–17]. In general, copper corrosion involves a simultaneous anodic dissolution and cathodic oxygen reduction reaction (ORR) process [18], and the involvement of a chemical reaction by oxygen molecule is suggested [19–23]. For example, Anderson et al. [22,23] indicated the increase in corrosion rate for copper by additional chemical attack between oxygen and cuprous ions. i.e.,

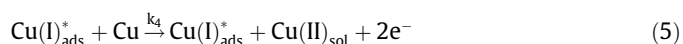
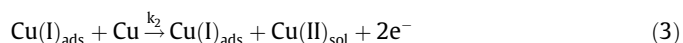


However, we found that the involvement of oxygen molecule seemed not able to explain the acceleration of electrochemical ORR in corrosion process suggested by electrochemical impedance spectroscopy (EIS) measurement. Our previous research ascribed a cathodic electrochemical ORR acceleration near the corrosion potential to a chemical redox between cuprous intermediate Cu(I)<sub>ads</sub><sup>\*</sup> and ORR intermediate (HO<sub>x</sub>)<sub>ads</sub><sup>\*</sup> synergistically, rather than oxygen molecule [24].

On the other hand, for copper electrodisolution in H<sub>2</sub>SO<sub>4</sub>, based on polarization curve and EIS measurements using a rotating disk

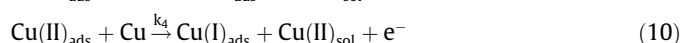
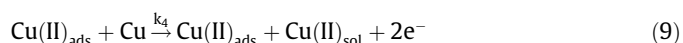
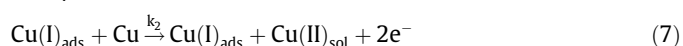
electrode (RDE) technique, Cordeiro et al. [25] used electrode kinetics study to propose a mechanism in deaerated solution (pH 0–5), i.e.,

At low anodic overpotential



where Cu(I)<sub>ads</sub> and Cu(I)<sub>ads</sub><sup>\*</sup> were absorbed cuprous species on electrode surface, and Cu(I)<sub>ads</sub><sup>\*</sup> was considered by Wong et al. [26] to be (bi)sulfate anion-associated, and could be desorbed and diffuse into the bulk solution. Copper was dissolved into solution via k<sub>4</sub> eventually.

At higher anodic overpotential



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Eqs. (2) and (4), (6) and (8) are pseudo-equilibrium reactions. Eqs. (3) and (5), (7) and (9) are autocatalytic reactions, with some intermediates playing a catalytic role and not consuming themselves. Moreover, two adsorbed species  $\text{Cu(I)}_{\text{ads}}$  and  $\text{Cu(II)}_{\text{ads}}$  were introduced to explain two faradaic capacitive loops. An inductive loop even rose when the quantity  $k_1 + k_{-1} - k_3 - 2k_2$  was negative, which was thought to be related to the surface coverage relaxation of  $\text{Cu(I)}_{\text{ads}}$  species. This mechanism was reasonable on the whole when the solution was deaerated, and it had been successfully used by some researchers to evaluate copper inhibitor [27,28]; however, when considering aerated solution, it seemed limited and needed to be modified.

To sum up, due to those discrepancies in cathodic ORR acceleration for corrosion process and deaerated schemes for electrodisolution process, mechanisms of copper corrosion and electrodisolution need to be clarified under more realistic condition (i.e. in naturally aerated  $\text{H}_2\text{SO}_4$  solution). In this work, the steady state (polarization curve) and non-steady state (electrochemical impedance) electrochemical measurements on copper were done in stagnant 0.5 M  $\text{H}_2\text{SO}_4$  with different dissolved oxygen content, in the potential range from  $-0.50$  up to  $0.15$  V vs. SCE. Polarization curves were compared among oxygenated, naturally aerated and deaerated experiments to analyze the influence of dissolved oxygen. Impedance and polarization data were compared between aerated and deaerated experiment, and mechanisms of copper corrosion and electrodisolution are proposed; three models are suggested and the experimental data are fitted accordingly. Finally, the dependence of the synergistic effect between chemical redox and electrochemical reaction on potential is indicated as well.

## 2. Experimental

Electrochemical measurements were conducted in a three-electrode cell at room temperature ( $20^\circ\text{C}$ ). Working electrode was prepared from a polyurethane-coated copper wire. Prior to an experiment, the polycrystalline copper wire was partly dipped into a hot 98%  $\text{H}_2\text{SO}_4$  solution for several minutes to remove the coating, yielding a section of bare glassy pure copper wire (99.9%) with a diameter of 1.64 mm. Next, its tip and lateral cylinder surface around the water line were enclosed with paraffin; consequently the working electrode was the lateral surface of a cylinder with a geometric area of  $4.48\text{ cm}^2$ . The sample was finally cleaned in double-distilled water. The newly prepared electrode was then inserted immediately into the 200 ml cell vertically for electrochemical reduction. Used as a counter electrode, a  $10\text{ cm}^2$  platinum sheet was placed parallel to the wire working electrode to guarantee creating an equipotential electric field enough, and a saturated calomel electrode (SCE) was used as reference electrode. All potentials reported here are referred to SCE.

In naturally aerated stagnant 0.5 M  $\text{H}_2\text{SO}_4$ , the copper electrode was held for 10 min at  $-0.70$  V vs. SCE to reduce the surface oxide film, reaching a current density of  $670\text{ }\mu\text{Acm}^{-2}$ , which came mainly from hydrogen evolution and a lot of hydrogen bubbles appeared. Then it was taken out to loose hydrogen bubbles absorbed at the electrode surface and immediately inserted into the electrolyte again, holding for 10 min at  $-0.60$  V vs. SCE, to reach a constant current density of nearly  $60\text{ }\mu\text{Acm}^{-2}$ . Because there were few hydrogen bubbles were observed on electrode surface, the ORR was thought as the main reaction process. Next, potentiodynamic polarization curve was collected in a positive direction from  $-0.60$  to  $0.15$  V vs. SCE at a scan rate of  $0.166\text{ mVs}^{-1}$ , using an EG&G PAR Model 273A Potentiostat /Galvanostat.

In contrast, prior to measurements in deaerated stagnant 0.5 M  $\text{H}_2\text{SO}_4$ , the solution was purged with nitrogen (99.9%) for 1 h. Subsequently, the working electrode was held for 20 min at  $-0.65$  V

vs. SCE to reduce the surface oxide film, reaching a current density of  $1.04\text{ mAcm}^{-2}$ , and then driven hydrogen bubbles away. After that, bubbling gas was stopped, approximately leaving 3% residual oxygen, and the cell was enclosed. The polarization curve was collected from  $-0.50$  to  $0.15$  V vs. SCE, and impedance measurements were carried out at given potentials corresponding to aerated experiments.

Similarly, before measurements in oxygenated stagnant 0.5 M  $\text{H}_2\text{SO}_4$ , the solution was aerated with oxygen (99.9%) for 20 min. Subsequently, the gas bubbling through the solution was stopped, and only a gas stream was flushed above the solution during the measurements. Next, a prepared copper wire electrode was prereduced at  $-0.7$  V vs. SCE for 20 min, driven away hydrogen bubbles; subsequently a potentiodynamic polarization curve was collected from  $-0.50$  to  $0.15$  V vs. SCE.

After polarization tests, solution ohmic resistance ( $R_s$ ) was measured by EIS at open circuit potential using an EG&G PAR Model 2263 Potentiostat /Galvanostat, which was the value of the real part of the impedance measured at the highest frequency. Polarization curves were corrected by subtracting the solution ohmic drop.

Before each impedance measurement, the prereduced (at  $-0.70$  V vs. SCE) copper electrode was held 3 ~ 5 min potentiostatically to reach the dc steady state at every given potential from  $-0.50$  to  $0.15$  V vs. SCE. Following that, all impedance experiments were done using ac signals with amplitude of  $\pm 5\text{ mV}$  at  $20\text{ mHz}$  ~  $100\text{ kHz}$  range, by an EG&G PAR Model 2263 Potentiostat/Galvanostat. Impedance data were collected using a PowerSuite Electrochemical Interface, and ac impedance spectra were analyzed by ZView2.80 software using nonlinear least squares (NLLS) fitting program [29].

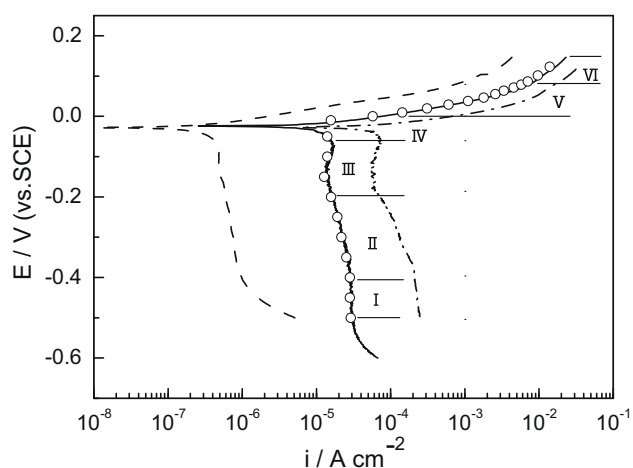
## 3. Results and discussion

### 3.1. Polarization measurements

Potentiodynamic polarization curves in oxygenated, naturally aerated and deaerated solution were displayed in Fig. 1. At the same time, potentiostatic polarization data before impedance measurements in naturally aerated solution were listed in Fig. 1, showing nearly the same stable currents with potentiodynamic ones. It is evidently noticed that the change in oxygen content will not influence the form of polarization curve; dissolved oxygen simultaneously accelerates cathodic and anodic reactions, resulting in almost the same corrosion potential. That is to say, oxygen plays a dual role as not only a cathodic reactant but an anodic accelerant as well. Aiming at these reaction characteristics, only deaerated and naturally aerated experiments were chosen to give a contrast.

Previously, in aerated solution, three cathodic ORR regions (I–III) were divided, and their impedance and polarization characteristics had been successfully analyzed [24]. At present, in aerated solution, another three regions are divided on polarization curve (see solid line in Fig. 1). Region IV ( $-0.05$ – $0$  V vs. SCE) is in the vicinity of corrosion potential (about  $-0.02$  V vs. SCE); Region V ( $0$ – $0.08$  V vs. SCE) represents the copper electrodisolution in the low anodic overpotential range; Region VI ( $0.08$ – $0.15$  V vs. SCE) is the electrodisolution in the high anodic overpotential range. Two different Tafel slopes (in Regions V and VI) are distinct.

In order to estimate how dissolved oxygen depends on the potential, here a preliminary comparison of current density is given in Table 1, at several potentials, i.e.,  $0.02$ ,  $0.04$ ,  $0.08$ ,  $0.12$ , and  $0.15$  V vs. SCE. From Table 1, it can be found that current density ratio  $i_{\text{ae}}/i_{\text{de}}$  decreases with the increase in anodic overpotential. This tendency probably indicates that the copper dissolution rate is dependent on not only dissolved oxygen, but also the potential, with less influence by dissolved oxygen at higher overpotentials.



**Fig. 1.** Potentiostatic polarization data in naturally aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> (○) and potentiodynamic polarization curves in oxygenated (---), naturally aerated (—) and deaerated (---) stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> (the last two are after Lu et al. [24]) on positive-going sweep on copper. Scan rate: 0.166 mV s<sup>-1</sup>. (I) Oxygen diffusion limiting current density region; (II) mixed kinetic-diffusion-controlled region; (III) hump phenomenon region; (IV) the region in the vicinity of corrosion potential; (V) low overpotential range; (VI) high overpotential range.

**Table 1**  
Comparison of electrochemical parameters between deaerated and aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

| <i>E</i> (V) | <i>i</i> <sub>ae</sub> (mA cm <sup>-2</sup> ) | <i>i</i> <sub>de</sub> (mA cm <sup>-2</sup> ) | <i>i</i> <sub>ae</sub> <sup>a</sup> / <i>i</i> <sub>de</sub> <sup>b</sup> | <i>R</i> <sub>ct,ae</sub> <sup>c</sup> / <i>R</i> <sub>ct,de</sub> <sup>d</sup> |
|--------------|-----------------------------------------------|-----------------------------------------------|---------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| 0.02         | 0.372                                         | 0.010                                         | 37.2                                                                      | 16.0                                                                            |
| 0.04         | 1.35                                          | 0.051                                         | 26.5                                                                      | 11.7                                                                            |
| 0.08         | 7.46                                          | 0.767                                         | 9.73                                                                      | 2.68                                                                            |
| 0.12         | 16.0                                          | 2.85                                          | 5.60                                                                      | 2.00                                                                            |
| 0.15         | 22.9                                          | 4.28                                          | 5.34                                                                      | 1.42                                                                            |

<sup>a,b</sup> *i*<sub>ae</sub> and *i*<sub>de</sub> denote the current density on potentiodynamic polarization curve at given potential in aerated and deaerated solutions.

<sup>c,d</sup> *R*<sub>ct,ae</sub> and *R*<sub>ct,de</sub> denote the charge-transfer resistance in aerated and deaerated solutions, which were calculated according to equivalent circuit of EIS at given potential.

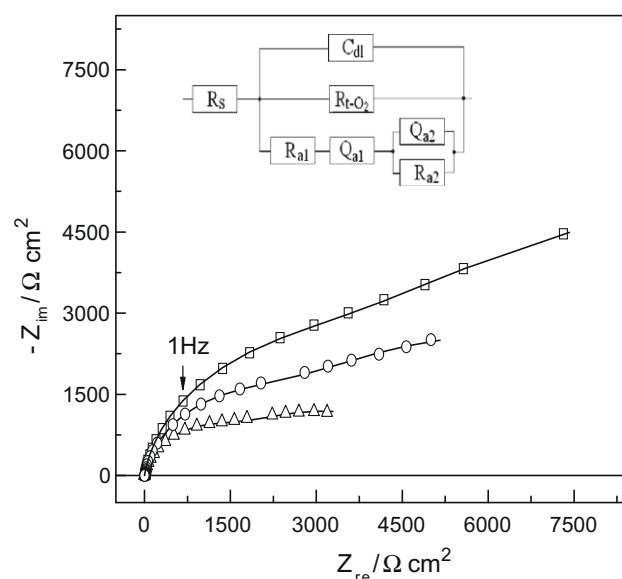
### 3.2. EIS measurements

#### 3.2.1. Reaction mechanism in Region IV

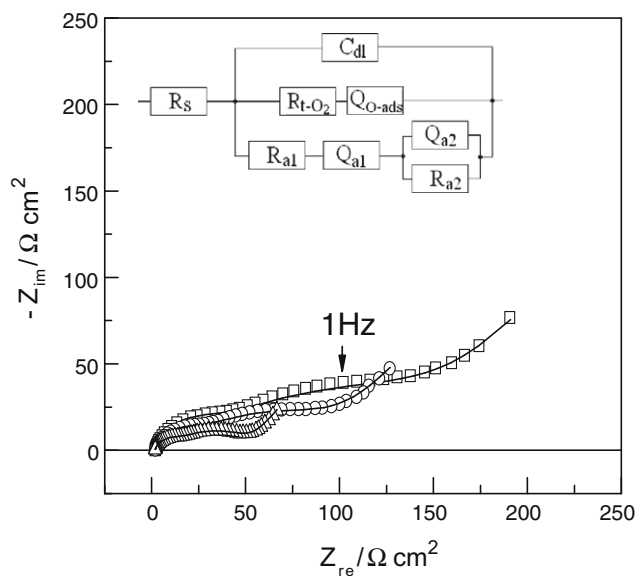
In Region IV, both anodic and cathodic processes have to be taken into account. Several typical impedance spectra (symbol) at given potentials are exhibited in Figs. 2 (the deaerated) and 3 (the aerated). A depressed high-and medium-frequency capacitive loop, followed by an obvious low-frequency diffusion behavior, is observed in Fig. 3; otherwise, the depressed capacitive loop seems to be coupled with low-frequency diffusion behavior in Fig. 2.

Normally, high-frequency capacitive loop is associated with the double layer charge-discharge process and rapid faradaic charge-transfer process [30–32]. However, the coupled high- and medium-frequency capacitive loop must be more complex, and be regarded as not only the relaxation of double layer and fast faradaic processes, probably but some medium rate ones, i.e., at least two time constants, we think.

With regard to consecutive dissolution reactions of metal, some researchers attributed the origin of a capacitive or an inductive behavior to the relaxation of surface coverage by an adsorbed intermediate [30–34]. In terms of Cordeiro et al., near the corrosion potential, the coupled high- and medium-frequency capacitive loop can be associated with the relaxation of surface coverage from Cu(I)<sub>ads</sub> as well as Cu(I)<sub>ads</sub><sup>\*</sup>. Finally, a copper dissolution mechanism

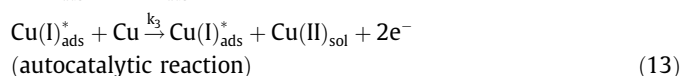


**Fig. 2.** Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in deaerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials: –0.02 (□); –0.01 (○); and 0 V (Δ) vs. SCE. The insert is the equivalent circuit model.

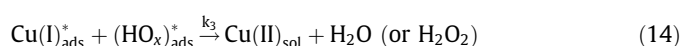


**Fig. 3.** Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in naturally aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials: –0.02 (□); –0.01 (○); and 0 V (Δ) vs. SCE. The insert is the equivalent circuit model.

associated with corrosion process in deaerated and aerated solutions is proposed (Model 1).



Concerning cathodic ORR near the corrosion potential [24], an additional chemical redox involved in aerated solution is given by



**Table 2**

Impedance parameters of copper at  $-0.02$  to  $0$  V vs. SCE in naturally deaerated stagnant  $0.5$  M  $\text{H}_2\text{SO}_4$ .

| $E$ (V) | $R_s$ ( $\Omega \text{ cm}^2$ ) | $C_{dl}$ ( $\mu\text{F cm}^{-2}$ ) | $R_{t-O_2}$ ( $\Omega \text{ cm}^2$ ) | $R_{a1}$ ( $\Omega \text{ cm}^2$ ) | $1/Y_{a1}^0$ ( $\Omega \text{ cm}^2$ ) | $n_{a1}$ | $Y_{a2}^0$ ( $\mu\text{F cm}^{-2}$ ) | $n_{a2}$ | $R_{a2}$ ( $\Omega \text{ cm}^2$ ) |
|---------|---------------------------------|------------------------------------|---------------------------------------|------------------------------------|----------------------------------------|----------|--------------------------------------|----------|------------------------------------|
| $-0.02$ | 1.67                            | 51.5                               | 18,653                                | 31.8                               | 3254                                   | 0.67     | 114                                  | 0.77     | 4143                               |
| $-0.01$ | 1.65                            | 53.5                               | 10,590                                | 27.2                               | 2668                                   | 0.65     | 119                                  | 0.80     | 2660                               |
| $0$     | 1.60                            | 52.8                               | 5273                                  | 20.8                               | 2120                                   | 0.65     | 135                                  | 0.79     | 1868                               |

Copper is dissolved into solution via  $k_3$ , Eq. (11) easily attains a pseudo-equilibrium, whereas unlike a reaction for RDE copper- $\text{H}_2\text{SO}_4$  system in Eq. (4), chemical process in Eq. (12) is not pseudo-equilibrium any more for stagnant copper- $\text{H}_2\text{SO}_4$  system, it involves some chemical processes, such as adsorption-desorption, or mass transfer process from electrode surface towards double layer or bulk solution, etc. And thus, its equivalent element may be of capacitive or diffusive characteristic, which is an important impedance behavior to discern  $\text{Cu(I)}_{\text{ads}}^*$  later.

Presence of an additional chemical redox (Eq. (14)) in Model 1 have no influence on the form of equivalent circuit, similar equivalent element are thereby compared to evaluate the reaction rate. Equivalent circuits (inserted graph) and fitting curves (solid line) are illustrated in Figs. 2 (the deaerated) and 3 (the aerated), and the fitting parameters are listed in Tables 2 and 3, respectively.

In equivalent circuits shown in Figs. 2 and 3, except  $R_s$ , cathodic elements  $R_{t-O_2}$  and  $Q_{O-ads}$  are in parallel to anodic ones, i.e.,  $R_{a1}$ ,  $Q_{a1}$ ,  $Q_{a2}$  and  $R_{a2}$ ; where  $R_s$  represents solution resistance;  $Q$  is a constant phase element (CPE) substituting for capacitive, diffusive or inductive element to give a more accurate fit, whose admittance and impedance are expressed as [35]:

$$Y = Y^0(j\omega)^n \quad (15)$$

$$\text{and } Z = (1/Y^0)(j\omega)^{-n} \quad (16)$$

where  $Y^0$  is the magnitude of  $Q$ ,  $\omega$  the angular frequency, and  $n$  the exponential term, which has many different explanations, it can be associated with the roughness of electrode surface [36], a distribution of reaction rates [37], non-uniform current distribution [38,39], etc. When  $n = 0.5$ ,  $Q$  is equivalent to  $W$ -Warburg impedance, a diffusive element; to resistance when  $n = 0$ ; to capacitance when  $n = 1$ , and to inductance when  $n = -1$ . However, when  $n$  is a medium value between them, it may indicate a relative and integrated influence by above factors, no longer a simple resistance, capacitance or diffusive element.

$R_{t-O_2}$  represents the charge-transfer resistance of forming ORR intermediates  $(\text{HO}_x)_{\text{ads}}^*$  from the reduction of oxygen molecules. Judging from  $n_{O-ads}$  (nearly 0.5),  $Q_{O-ads}$  is the CPE representing the diffusion of desorbed  $(\text{HO}_x)_{\text{ads}}^*$  towards double layer or bulk solution to proceed the chemical redox, which is omitted in the equivalent circuit of Fig. 2 because of absolute cathodic kinetic-controlled mechanism in deaerated solution, asserted by Quartarone et al. [19,20].

Comparing  $R_{t-O_2}$  in Table 2 with Table 3, the former is a factor of nearly one hundred greater than the latter, verifying the difficulty of the ORR in deaerated solution. Additionally, similar to synergistic effect in cathodic hump range, additional chemical redox (Eq. (14)) promotes electrochemical reduction of oxygen, making  $R_{t-O_2}$  in Table 3 decrease as potential moves positively, so does

$R_{t-O_2}$  in Table 2 due to the presence of a trace amount of dissolved oxygen. Obviously, it is more reasonable to correlate chemical redox with ORR intermediates, not oxygen molecule.

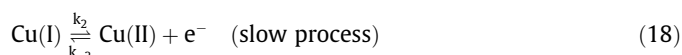
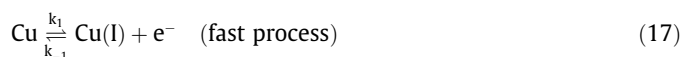
In addition,  $R_{a1}$  is the charge-transfer resistance of Cu dissolution to  $\text{Cu(I)}_{\text{ads}}$  (Eq. (11)), a reversible pseudo-equilibrium process, which always keeps small in Tables 2 and 3. For  $n_{a1} \approx 0.5$ , the constant phase element  $Q_{a1}$  is linked to a diffusion process between  $\text{Cu(I)}_{\text{ads}}$  and  $\text{Cu(I)}_{\text{ads}}^*$  via Eq. (12). Parallel arrangement of  $R_{a2}$ – $Q_{a2}$  is used to describe the process of Eq. (13),  $R_{a2}$  is the charge-transfer resistance of  $\text{Cu(I)}_{\text{ads}}^*$  oxidization to  $\text{Cu(II)}_{\text{sol}}$ ,  $Q_{a2}$  is the CPE resembling a pseudo-capacitance for  $n_{a2}$  near to 1. Comparing Table 2 with Table 3, when  $R_{a2}$  is small, such as in aerated solution (see Table 3), it reveals the acceleration of electrochemical reaction (Eq. (13)) by chemical redox (Eq. (14)).

From  $1/Y_{a1}^0 \gg R_{a2}$  in Table 3, a diffusion-controlled step is suggested in aerated solution; but a mixed kinetic-diffusion determining step is indicated in deaerated solution ( $1/Y_{a1}^0$  is comparable with  $R_{a2}$  in Table 2), therefore the different low-frequency impedance characteristics are observed in Figs. 2 and 3, respectively.

As discussed above, the determining step of the corrosion rate in aerated  $\text{H}_2\text{SO}_4$  solution can be easily concluded. Cathodic charge-transfer resistance  $R_{t-O_2}$  is comparable with anodic diffusion resistance  $1/Y_{a1}^0$  in Table 3, thus the corrosion rate is controlled by cathodic kinetics process, together with anodic mass transport process.

### 3.2.2. Anodic electrodisolution at low overpotential in Reg. V

Mattsson and Bockris proposed two reversible reactions to account for steady state results [40], i.e.,



However, according to literature [41,42], if either reaction became slow enough to be irreversible, the overall reaction rate would be controlled by different step relating to potential, a low and a high Tafel slope can probably be predicted on  $E$ – $I$  curve. Consequently, two Tafel slopes of about  $40 \text{ mV dec}^{-1}$  and  $140 \text{ mV dec}^{-1}$  are always observed [25,43].

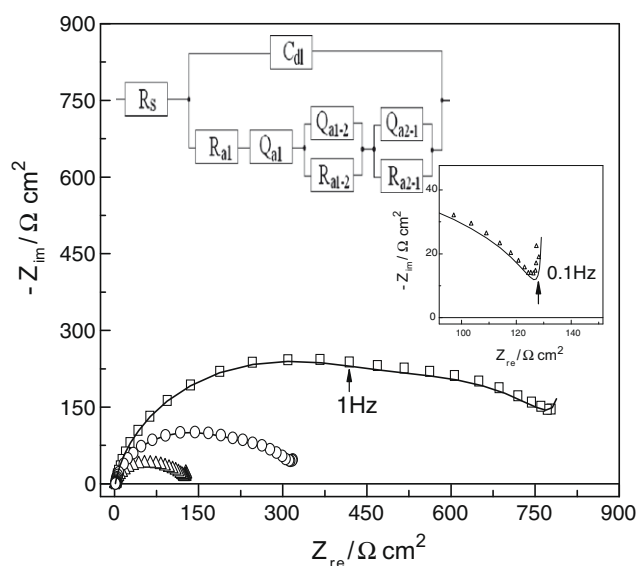
A lower Tafel slope is observed at region V in Fig. 1, and impedance results (symbol) are presented in Figs. 4 (the deaerated) and 5 (the aerated). Both have a depressed capacitive loop in high- and medium-frequency range. In contrast with Fig. 5, the loop radius in Fig. 4 is far large, suggesting a slower anodic dissolution rate in deaerated solution. Additionally, an inductive loop at  $1 \text{ Hz}$  independent of potential, followed by a low-frequency faradaic capacitive loop with diffusion characteristic is observed in Fig. 5, whereas only a low-frequency diffusion behavior occurs in Fig. 4.

**Table 3**

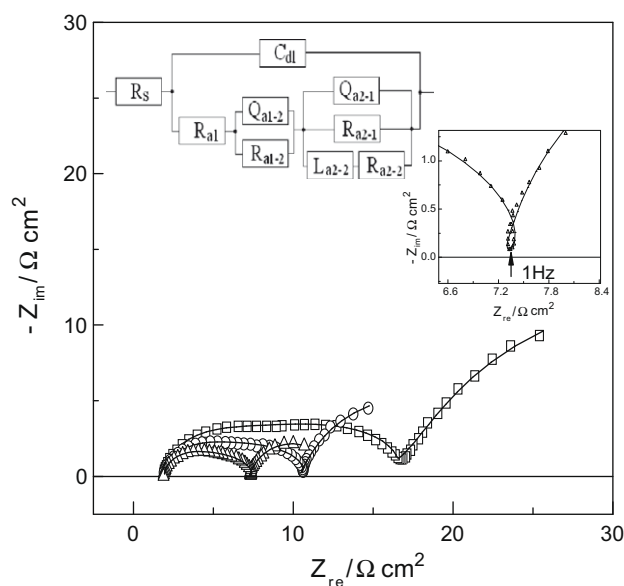
Impedance parameters of copper at  $-0.02$  to  $0$  V vs. SCE in naturally aerated stagnant  $0.5$  M  $\text{H}_2\text{SO}_4$ .

| $E$ (V) | $R_s$ ( $\Omega \text{ cm}^2$ ) | $C_{dl}$ ( $\mu\text{F cm}^{-2}$ ) | $R_{t-O_2}$ ( $\Omega \text{ cm}^2$ ) | $1/Y_{O-ads}^0$ ( $\Omega \text{ cm}^2$ ) | $n_{O-ads}$ | $R_{a1}$ ( $\Omega \text{ cm}^2$ ) | $1/Y_{a1}^0$ ( $\Omega \text{ cm}^2$ ) | $n_{a1}$ | $Y_{a2}^0$ ( $\mu\text{F cm}^{-2}$ ) | $n_{a2}$ | $R_{a2}$ ( $\Omega \text{ cm}^2$ ) |
|---------|---------------------------------|------------------------------------|---------------------------------------|-------------------------------------------|-------------|------------------------------------|----------------------------------------|----------|--------------------------------------|----------|------------------------------------|
| $-0.02$ | 1.94                            | 32.1                               | 187.6                                 | 24.7                                      | 0.62        | 10.7                               | 385.9                                  | 0.48     | 143.5                                | 0.88     | 16.7                               |
| $-0.01$ | 1.93                            | 35.1                               | 109.9                                 | 16.7                                      | 0.59        | 9.0                                | 368.6                                  | 0.52     | 197.4                                | 0.87     | 12.2                               |
| $0$     | 1.93                            | 37.7                               | 53.0                                  | 7.8                                       | 0.61        | 6.9                                | 384.2                                  | 0.58     | 265.5                                | 0.86     | 7.0                                |





**Fig. 4.** Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in deaerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials: 0.02 (□); 0.03 (○); and 0.04 V (Δ) (including an enlarged graph) vs. SCE. The insert is the equivalent circuit model.



**Fig. 5.** Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in naturally aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials: 0.02 (□); 0.03 (○); and 0.04 V (Δ) (including an enlarged graph) vs. SCE. The insert is the equivalent circuit model.

According to literature [25,27,28], low-frequency faradaic capacitive loop is normally related to the relaxation process of cupric adsorption intermediate Cu(II)<sub>ads</sub>, which seems to easily occur in aerated solution.

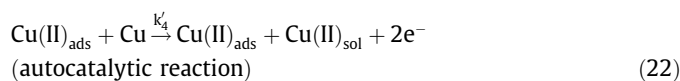
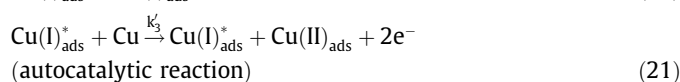
It is realistic not to consider the influences of the cathodic ORR species from now on, owing to increased anodic current in aerated solution and slow ORR from the trace amount of dissolved oxygen in deaerated solution. Needless to say, it can no longer consider the ORR intermediates, and makes the participation of oxygen molecule inevitably.

Cuprous intermediates are easily catalyzed by oxygen species into cupric species [22,23,44–48]. According to Cordeiro et al., in

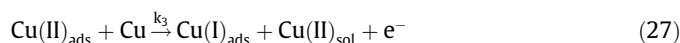
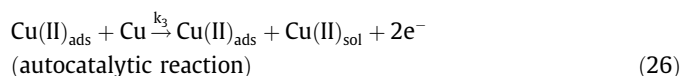
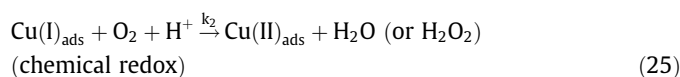
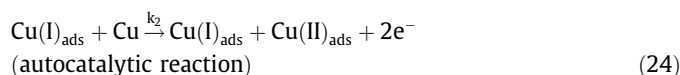
deaerated and RDE copper–H<sub>2</sub>SO<sub>4</sub> system, Cu(I)<sub>ads</sub> and Cu(I)<sub>ads</sub><sup>\*</sup> were principal adsorption intermediate at low overpotentials [25], so were Cu(I)<sub>ads</sub> and Cu(II)<sub>ads</sub> at high overpotentials, which seemed reasonable considering Mattson and Bockris' two consecutive-step theory [40]. Nevertheless, with the limitation of mass transfer and potential in deaerated and stagnant copper–H<sub>2</sub>SO<sub>4</sub> system, the adsorption intermediates Cu(I)<sub>ads</sub>, Cu(I)<sub>ads</sub><sup>\*</sup> and Cu(II)<sub>ads</sub> may become a transitional state, which involves some adsorption–desorption and slow diffusion chemical processes, etc. On contrary, in aerated and stagnant copper–H<sub>2</sub>SO<sub>4</sub> system, because of the combination with synergistic acceleration by chemical redox relevant to oxygen molecules on surface, Cu(I)<sub>ads</sub> and Cu(II)<sub>ads</sub> can presumably become predominant intermediates.

The presence of inductive loop is always hard to explain. Some researchers explained it as relaxation of adsorption–desorption of intermediate species [25,31,33], Cordeiro et al. considered it as a relaxation of surface coverage of Cu(I)<sub>ads</sub>. Similarly, the inductive loop at 1 Hz occurring from 0.02 V vs. SCE in Fig. 5 is related with the relaxation process between Cu(I)<sub>ads</sub> and Cu(II)<sub>ads</sub>. Therefore, electrodisolution mechanisms (Model 2) at low overpotentials in both solutions are as follows:

In deaerated solution



In aerated solution



Copper is dissolved into solution via  $k_4$  in deaerated solution and via  $k_3$  in aerated solution. Accordingly, equivalent circuits (inserted graph) and fitting curves (solid line) are displayed in Figs. 4 (the deaerated) and 5 (the aerated). Meanwhile, the fitting parameters are listed in Tables 4 and 5, respectively.

In equivalent circuit of Fig. 4,  $R_{a1}$  and  $Q_{a1}$  have the same physical meanings as before, a charge-transfer resistance via Eq. (19) and a CPE of Eq. (20). Paralleled  $R_{a1-2} - Q_{a1-2}$  elements represent the charge-transfer resistance and CPE of Cu(I)<sub>ads</sub><sup>\*</sup> oxidation to Cu(II)<sub>ads</sub> via Eq. (21). Additionally, paralleled  $R_{a2-1} - Q_{a2-1}$  elements represent the charge-transfer resistance and CPE of autocatalytic reaction via Eq. (22).  $Q_{a2-1}$  represents mass transport behavior from  $n_{a2-1} \approx 0.5$ , and therefore corresponds to the low-frequency diffusion in Fig. 4.

In equivalent circuit of Fig. 5, except  $R_{a1-2}$  and  $Q_{a1-2}$  (charge-transfer resistance and CPE of Cu(I)<sub>ads</sub> oxidation to Cu(II)<sub>ads</sub> via Eq. (24)),  $R_{a1}$  (charge-transfer resistance via Eq. (23)),  $R_{a2-1}$  and  $Q_{a2-1}$  (charge-transfer resistance and CPE relating to Eq. (26)), have

**Table 4**Impedance parameters of copper at 0.02 to 0.04 V vs. SCE in naturally deaerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub>.

| <i>E</i> (V) | <i>R</i> <sub>s</sub> (Ω cm <sup>2</sup> ) | <i>C</i> <sub>dl</sub> (μF cm <sup>-2</sup> ) | <i>R</i> <sub>a1</sub> (Ω cm <sup>2</sup> ) | <i>Y</i> <sub>a1</sub> <sup>0</sup> (F cm <sup>-2</sup> ) | <i>n</i> <sub>a1</sub> | <i>Y</i> <sub>a1-2</sub> <sup>0</sup> (mF cm <sup>-2</sup> ) | <i>n</i> <sub>a1-2</sub> | <i>R</i> <sub>a1-2</sub> (Ω cm <sup>2</sup> ) | 1/ <i>Y</i> <sub>a2-1</sub> <sup>0</sup> (Ω cm <sup>2</sup> ) | <i>n</i> <sub>a2-1</sub> | <i>R</i> <sub>a2-1</sub> (Ω cm <sup>2</sup> ) |
|--------------|--------------------------------------------|-----------------------------------------------|---------------------------------------------|-----------------------------------------------------------|------------------------|--------------------------------------------------------------|--------------------------|-----------------------------------------------|---------------------------------------------------------------|--------------------------|-----------------------------------------------|
| 0.02         | 1.65                                       | 63.16                                         | 14.95                                       | 0.06                                                      | 0.95                   | 2.82                                                         | 0.88                     | 269.8                                         | 6672                                                          | 0.73                     | 520.5                                         |
| 0.03         | 1.62                                       | 69.24                                         | 11.89                                       | 0.12                                                      | 0.97                   | 4.27                                                         | 0.85                     | 87.8                                          | 4251                                                          | 0.70                     | 224.6                                         |
| 0.04         | 1.62                                       | 75.43                                         | 8.60                                        | 0.29                                                      | 1.00                   | 8.60                                                         | 0.84                     | 23.2                                          | 1985                                                          | 0.64                     | 96.8                                          |

**Table 5**Impedance parameters of copper at 0.02–0.04 V vs. SCE in naturally aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub>.

| <i>E</i> (V) | <i>R</i> <sub>s</sub> (Ω cm <sup>2</sup> ) | <i>C</i> <sub>dl</sub> (μF cm <sup>-2</sup> ) | <i>R</i> <sub>a1</sub> (Ω cm <sup>2</sup> ) | <i>Y</i> <sub>a1-2</sub> <sup>0</sup> (F cm <sup>-2</sup> ) | <i>n</i> <sub>a1-2</sub> | <i>R</i> <sub>a1-2</sub> (Ω cm <sup>2</sup> ) | 1/ <i>Y</i> <sub>a2-1</sub> <sup>0</sup> (Ω cm <sup>2</sup> ) | <i>n</i> <sub>a2-1</sub> | <i>R</i> <sub>a2-1</sub> (Ω cm <sup>2</sup> ) | <i>L</i> <sub>a2-2</sub> (H cm <sup>2</sup> ) | <i>R</i> <sub>a2-2</sub> (Ω cm <sup>2</sup> ) |
|--------------|--------------------------------------------|-----------------------------------------------|---------------------------------------------|-------------------------------------------------------------|--------------------------|-----------------------------------------------|---------------------------------------------------------------|--------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 0.02         | 1.94                                       | 57.83                                         | 3.86                                        | 0.60                                                        | 0.78                     | 32.19                                         | 114.94                                                        | 0.49                     | 14.24                                         | 9.43                                          | 67.33                                         |
| 0.03         | 1.93                                       | 59.74                                         | 2.87                                        | 1.09                                                        | 0.83                     | 13.35                                         | 119.05                                                        | 0.52                     | 7.24                                          | 3.01                                          | 32.49                                         |
| 0.04         | 1.94                                       | 64.63                                         | 2.50                                        | 1.82                                                        | 0.88                     | 5.23                                          | 163.93                                                        | 0.62                     | 3.41                                          | 1.00                                          | 19.03                                         |

the same physical meanings as those in Fig. 4. Besides, the series arrangements of  $L_{a2-2}$ – $R_{a2-2}$  are an inductive element and a charge-transfer resistance of non-autocatalytic reaction via Eq. (27), here  $L_{a2-2}$  represents lagged relaxation of the surface adsorbed intermediates between Cu(I)<sub>ads</sub> and Cu(II)<sub>ads</sub>; i.e., Cu(II)<sub>ads</sub> is consumed to form Cu(I)<sub>ads</sub> from Eq. (27), and subsequently, Cu(I)<sub>ads</sub> is consumed to regenerate Cu(II)<sub>ads</sub> via Eqs. (24) and (25), resembling an inductance to baffle the dc current in circuit. From  $n_{a2-1}$  (nearly 0.5), low-frequency diffusion characteristic can be explained.

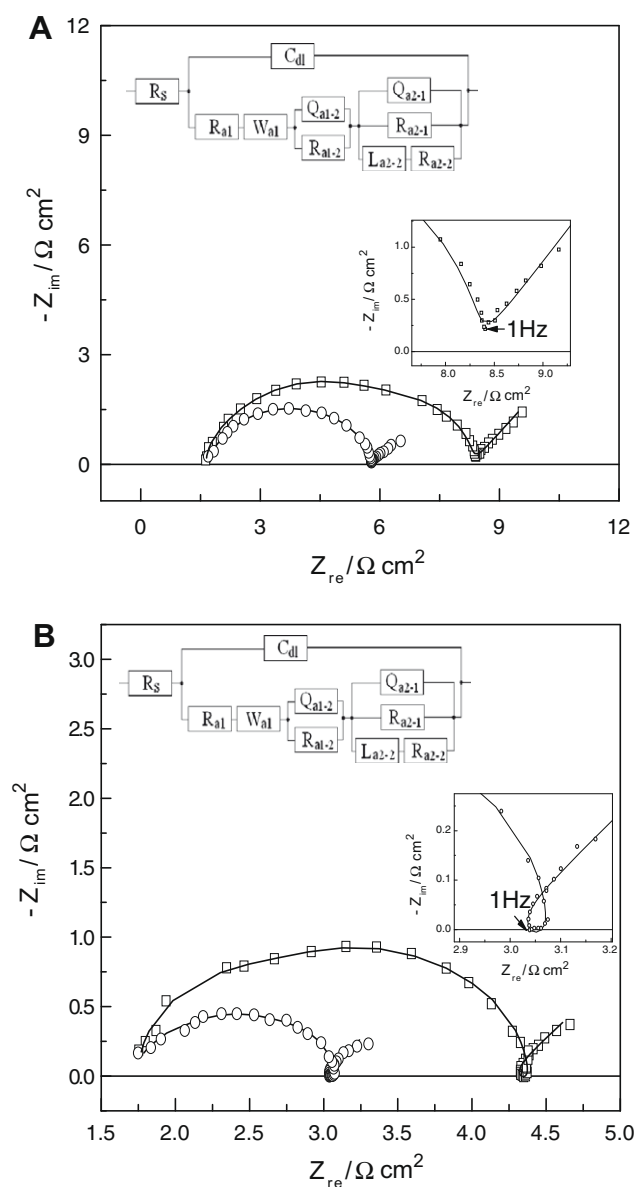
In Table 4,  $R_{a2-1} > R_{a1-2} > R_{a1}$ , indicating that reaction via Eq. (19) is the fastest, the reaction via Eq. (22) the slowest one. Furthermore, as potential goes positively,  $R_{a2-1}$  and  $R_{a1-2}$  decrease quickly, finally close to  $R_{a1}$ , suggesting that the formation of cupric species is more sensitive to potential than that of cuprous species.

In Table 5,  $R_{a2-2} > R_{a1-2} > R_{a2-1} > R_{a1}$ , indicating that the reaction via Eq. (23) is the fastest, and the reaction with inductive behavior via Eq. (27) is the slowest. Moreover,  $R_{a2-1}$  in Table 5 is a factor of nearly 30 times less than that in Table 4,  $1/Y_{a2-1}^0$  in Table 5 is a factor of tens times less than that in Table 4, confirming a synergistic acceleration by electrochemical oxidation (Eq. (24)) and chemical redox (Eq. (25)) jointly. Moreover, the similar potential dependence is observed, the formation rate of cupric species ( $R_{a1-2}$  and  $R_{a2-1}$ ) approaches that of cuprous species ( $R_{a1}$ ) with the increase in anodic overpotential. As for inductive element  $L_{a2-2}$ , its presence can be derived from chemical redox and potential, and it diminishes with the decrease in  $R_{a2-2}$ ,  $R_{a1-2}$  and  $R_{a2-1}$  as potential moves positively, indicating of weakened retarding effect on dc and less dependence on chemical redox.

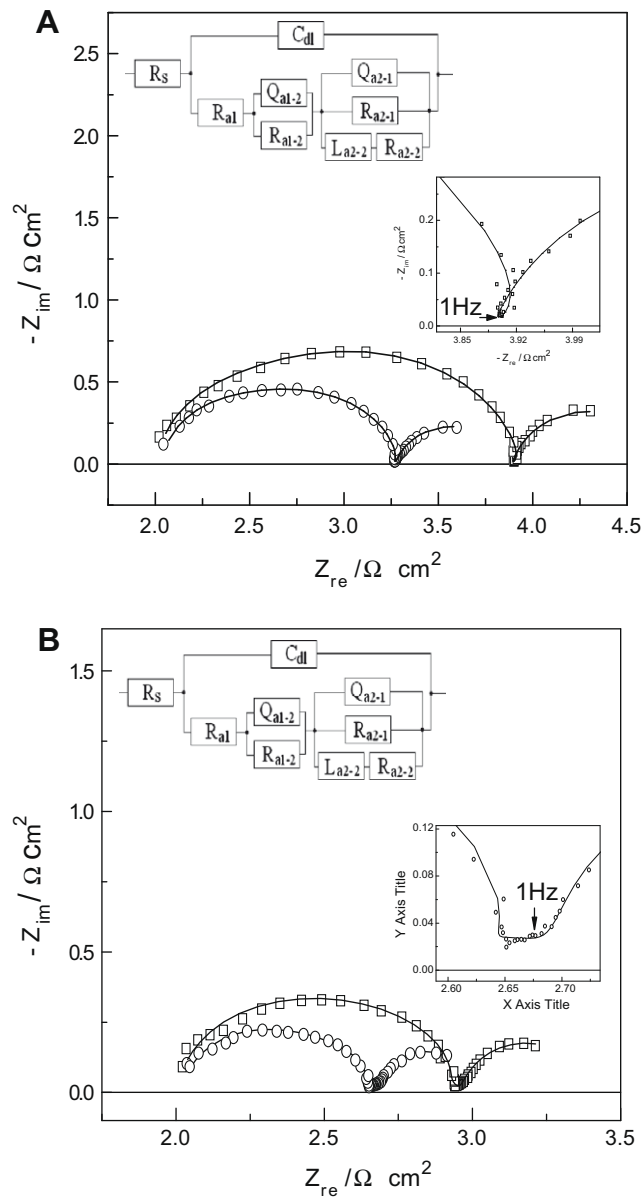
### 3.2.3. Anodic dissolution at high overpotential in Region VI

Similarly, a higher Tafel slope is observed in region VI of Fig. 1 at high overpotentials, and impedance spectra (symbol) can be obtained in Figs. 6 (the deaerated) and 7 (the aerated). The same impedance characteristic of a high- and medium-frequency capacitive loop and an inductive loop at 1 Hz, followed by a low-frequency capacitive loop can be observed in Figs. 6 and 7. Nevertheless, the inductive loop does not appear until 0.08 V vs. SCE in deaerated solution (Fig. 6), while it disappears from 0.15 V vs. SCE in aerated solution (Fig. 7). Furthermore, contrasted to a low-frequency capacitive behavior in Fig. 7, a low-frequency diffusion characteristic seems more distinct in Fig. 6.

As expected, formation rate of cupric species can be equal to or even surpass those of cuprous species as potential moves positively [25], which probably changes the reaction rate and Tafel slope. As a result, Model 3 at high overpotentials is proposed.

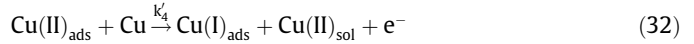
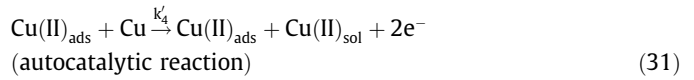
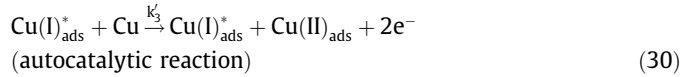


**Fig. 6.** Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in deaerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials: (A) 0.08 (□) (including an enlarged graph) and 0.10 V (○); (B) 0.12 (□) and 0.15 V (○) (including an enlarged graph) vs. SCE. The insert is the equivalent circuit model.

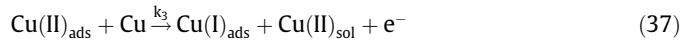
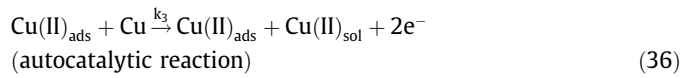
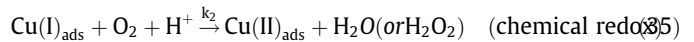
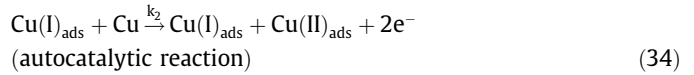


**Fig. 7.** Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials: (A) 0.08 (□) and 0.10 V (○) (including an enlarged graph); (B) 0.12 (□) and 0.15 V (○) (including an enlarged graph) vs. SCE. The insert is the equivalent circuit model.

In deaerated solution



In aerated solution



Copper is dissolved into solution via  $k'_4$  in deaerated solution and via  $k_3$  in aerated solution. Contrasted with Model 2, formations of  $\text{Cu(I)}_{\text{ads}}$  in deaerated solution (Eq. (28)) and in aerated solution (Eq. (32)) in Model 3 become irreversible.

Accordingly, equivalent circuits (inserted graph) and fitting curves (solid line) are displayed in Figs. 6 (the deaerated) and 7 (the aerated), their fitting parameters are listed in Tables 6 and 7, respectively.

In Figs. 6 and 7, all equivalent elements have the same physical meanings as before, except that  $Q_{a1}$  in Fig. 4 is substituted by a diffusive element  $W_{a1}$  in Fig. 6, which is still supposed to represent chemical process between  $\text{Cu(I)}_{\text{ads}}$  and  $\text{Cu(I)}^*_{\text{ads}}$  (Eq. (29)).

In Tables 6 and 7, as predicted,  $R_{a1-2}$  and  $R_{a2-1}$  are almost equal to or even less than  $R_{a1}$ . Therefore, irreversible reactions via Eqs. (28) and (32) in Model 3 are verified. What is more, though  $R_{a2-2}$  is still the largest one, it decreases quickly and approaches the other three resistances (i.e.,  $R_{a1}$ ,  $R_{a1-2}$  and  $R_{a2-1}$ ), suggesting a fast rate in each way. As for inductive element  $L_{a2-2}$ , it progressively diminishes with the decrease in  $R_{a1-2}$ ,  $R_{a2-1}$  and  $R_{a2-2}$ .

Comparing  $R_{a2-1}$  and  $1/Y_{a2-1}^0$  in Tables 7 with those in 6, less difference is observed. It is confirmed that the formation rate of cupric species is now far more influenced by the potential, other than chemical redox, in agreement with the comparison of current density in Table 1.

### 3.2.4. Comparison in charge-transfer resistances in Region IV-VI

By now, charge-transfer resistances at different potentials in deaerated ( $R_{ct,de}$ ) and aerated ( $R_{ct,ae}$ ) solution can be calculated, in light of proposed equivalent circuits. Consequently, the resistance ratios denoted as  $R_{ct,de}/R_{ct,ae}$  are listed in Table 1. From Table 1, resistance ratio  $R_{ct,de}/R_{ct,ae}$  and current density ratio  $i_{ae}/i_{de}$  have the same tendency, they both decrease with potential increasing. That is to say, synergistic effect involving dissolved oxygen is weakened with higher overpotential.

**Table 6**  
Impedance parameters of copper in deaerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub>: (A) at 0.08–0.10 V; (B) at 0.12–0.15 V vs. SCE.

| E (V) | $R_s$ ( $\Omega \text{ cm}^2$ ) | $C_{dl}$ ( $\mu\text{F cm}^{-2}$ ) | $R_{a1}$ ( $\Omega \text{ cm}^2$ ) | $1/Y_{a1}^0$ ( $\Omega \text{ cm}^2$ ) | $Y_{a1-2}^0$ ( $\text{mF cm}^{-2}$ ) | $n_{a1-2}$ | $R_{a1-2}$ ( $\Omega \text{ cm}^2$ ) | $Y_{a2-1}^0$ ( $\text{mF cm}^{-2}$ ) | $n_{a2-1}$ | $R_{a2-1}$ ( $\Omega \text{ cm}^2$ ) | $L_{a2-2}$ (H $\text{cm}^2$ ) | $R_{a2-2}$ ( $\Omega \text{ cm}^2$ ) |
|-------|---------------------------------|------------------------------------|------------------------------------|----------------------------------------|--------------------------------------|------------|--------------------------------------|--------------------------------------|------------|--------------------------------------|-------------------------------|--------------------------------------|
| (A)   |                                 |                                    |                                    |                                        |                                      |            |                                      |                                      |            |                                      |                               |                                      |
| 0.08  | 1.65                            | 91.74                              | 2.34                               | 0.77                                   | 4.09                                 | 0.98       | 1.27                                 | 1.05                                 | 0.85       | 3.08                                 | 7.17                          | 42.86                                |
| 0.10  | 1.69                            | 93.53                              | 1.47                               | 0.36                                   | 2.59                                 | 0.99       | 1.03                                 | 2.76                                 | 0.86       | 1.50                                 | 1.67                          | 20.20                                |
| (B)   |                                 |                                    |                                    |                                        |                                      |            |                                      |                                      |            |                                      |                               |                                      |
| 0.12  | 1.74                            | 106.78                             | 1.39                               | 0.21                                   | 4.29                                 | 1.00       | 0.55                                 | 0.60                                 | 0.93       | 0.77                                 | 0.47                          | 3.61                                 |
| 0.15  | 1.74                            | 115.18                             | 0.64                               | 0.14                                   | 3.61                                 | 1.00       | 0.32                                 | 0.62                                 | 1.00       | 0.36                                 | 0.11                          | 1.23                                 |



**Table 7**Impedance parameters of copper in aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub>: (A) at 0.08–0.10 V; (B) at 0.12–0.15 V vs. SCE.

| <i>E</i> (V) | <i>R</i> <sub>s</sub> (Ω cm <sup>2</sup> ) | <i>C</i> <sub>dl</sub> (μF cm <sup>-2</sup> ) | <i>R</i> <sub>a1</sub> (Ω cm <sup>2</sup> ) | <i>Y</i> <sub>a1-2</sub> <sup>0</sup> (F cm <sup>-2</sup> ) | <i>n</i> <sub>a1-2</sub> | <i>R</i> <sub>a1-2</sub> (Ω cm <sup>2</sup> ) | <i>Y</i> <sub>a2-1</sub> <sup>0</sup> (mF cm <sup>-2</sup> ) | <i>n</i> <sub>a2-1</sub> | <i>R</i> <sub>a2-1</sub> (Ω cm <sup>2</sup> ) | <i>L</i> <sub>a2-2</sub> (H cm <sup>2</sup> ) | <i>R</i> <sub>a2-2</sub> (Ω cm <sup>2</sup> ) |
|--------------|--------------------------------------------|-----------------------------------------------|---------------------------------------------|-------------------------------------------------------------|--------------------------|-----------------------------------------------|--------------------------------------------------------------|--------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| (A)          |                                            |                                               |                                             |                                                             |                          |                                               |                                                              |                          |                                               |                                               |                                               |
| 0.08         | 2.02                                       | 96.05                                         | 0.94                                        | 7.14                                                        | 0.86                     | 0.80                                          | 2.0                                                          | 0.79                     | 0.99                                          | 0.35                                          | 17.04                                         |
| 0.10         | 2.04                                       | 124.87                                        | 0.72                                        | 9.09                                                        | 0.82                     | 0.60                                          | 2.5                                                          | 0.83                     | 0.53                                          | 0.064                                         | 9.74                                          |
| (B)          |                                            |                                               |                                             |                                                             |                          |                                               |                                                              |                          |                                               |                                               |                                               |
| 0.12         | 2.01                                       | 194.39                                        | 0.43                                        | 11.11                                                       | 0.86                     | 0.44                                          | 67.57                                                        | 0.62                     | 0.62                                          | 0.012                                         | 3.21                                          |
| 0.15         | 2.02                                       | 311.14                                        | 0.23                                        | 16.67                                                       | 1.00                     | 0.28                                          | 11.15                                                        | 0.42                     | 0.64                                          | 0.0084                                        | 1.59                                          |

#### 4. Conclusion

Compared with deaerated results, mechanisms of copper corrosion and electrodisolution in naturally aerated stagnant 0.5 M H<sub>2</sub>SO<sub>4</sub> are clarified in detail. The influence by dissolved oxygen is suggested, and three reaction mechanism models are proposed. The experimental results are quantitatively fitted, and an excellent agreement is found.

Near to corrosion potential, electrochemical dissolution of copper is accelerated by chemical redox between cuprous intermediate and ORR intermediate in double layer or bulk solution synergistically. Corrosion rate is thereby controlled by cathodic kinetic and anodic mass transfer process.

In the region of anodic electrodisolution, overall reaction rate is controlled by different rate steps changing with the potential, resulting in the presence of a low Tafel slope and a high Tafel slope. Contrasted to deaerated results, electrochemical reactions in aerate solution are accelerated by additional chemical redox between oxygen molecules and adsorbed cuprous interfacial species at the electrode surface.

By analyzing polarization and impedance results, it can be concluded that the influence of dissolved oxygen depends on the potential. The synergetic effect involving chemical redox by dissolved oxygen is weakened with higher anodic overpotential.

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