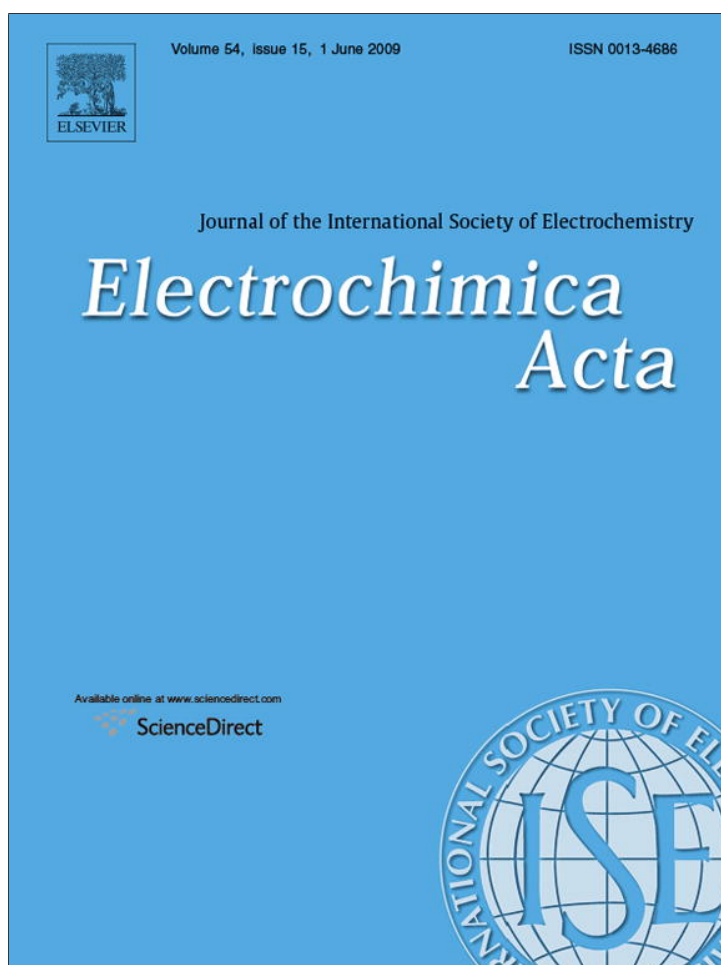




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journal homepage: www.elsevier.com/locate/electactaOxygen reduction mechanism on copper in a 0.5 M H₂SO₄Yonghong Lu^a, Haibo Xu^{a,*}, Jia Wang^{a,b}, Xiangfeng Kong^a^a Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, 238 Songling Road, Qingdao 266100, Shandong Province, China^b State Key Laboratory for Corrosion and Protection of Metals, Shenyang 110016, China

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ABSTRACT

The mechanism of the oxygen reduction reaction (ORR) in a naturally aerated stagnant 0.5 M H₂SO₄ was studied using electrochemical methods. The cathodic polarization curve showed three different regions; electrochemical impedance spectroscopy (EIS) measurement was used accordingly. The EIS data were analyzed, and the mechanism for the ORR was proposed consequently. The three regions include a limiting current density region with the main transfer of 4e[−] controlled by diffusion (−0.50 V < E < −0.40 V), a combined kinetic-diffusion region (−0.40 V < E < −0.20 V) with an additional 2e[−] transfer due to the adsorption of the anions, and a hump phenomenon region (−0.20 V < E < −0.05 V), in which the chemical redox between the anodic intermediate Cu(I)_{ads}^{*} and the cathodic intermediate (HO_x)_{ads}^{*}, together with the electrochemical reaction, synergistically results in the acceleration of the ORR. Therefore, a coupled electrochemical/chemical process (the EC mechanism) in the hump phenomenon region was proposed, and a good agreement was found between the experimental and fitted results. The EC mechanism was confirmed by the deaerated experiments.

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1. Introduction

Copper and its alloys are used extensively in many types of chemical equipment and industries [1,2]. Moreover, their application frequently involves acidic solutions and dissolved oxygen. Generally, except under high cathodic overpotentials, copper does not displace hydrogen, and the presence of dissolved oxygen is essential for its cathodic reduction [3–5]. Therefore, it is important to investigate the mechanism of the oxygen reduction reaction (ORR) on copper in acidic solutions, and a lot of work has been done in this regard [5–9].

The reduction of oxygen may occur via a 4e[−] (Eq. (1)), a 2e[−] (Eq. (2)), or a mixed process that combines these two limiting cases [10,11].



Eqs. (1) and (2) involve many elementary reactions and are strongly influenced by potential [11]. Moreover, they generally relate to the electrode surface state and the adsorption of the anions; additionally, they may be catalyzed by the cuprous species

in the medium [12–16]. The pathway of the ORR and the specific adsorption of the anions on polycrystalline and single crystalline copper surfaces in H₂SO₄ have been investigated by electrochemical and spectroscopic analysis techniques [4,7–9,17–20]. However, the influence of the anodic reaction is usually neglected in the investigation except when considering the catalytic effect from the cuprous species. Furthermore, some researchers have found and explained the hump phenomenon on copper in H₂SO₄ near the corrosion potential [12,21,22], which exerts a strong influence on the corrosion rate and inhibition efficiency. However, the mechanism of the ORR remains the subject of some uncertainty and dispute [4,7,22,23], and a comprehensive and thorough investigation is necessary.

The EIS method has been successfully used to study the anodic and cathodic reaction mechanisms of the metal [21,22,24–28]. It is useful in deriving quantitative kinetic information on the electrode surface [29–31]. In our work, the polarization curve was measured to determine the general characteristics of the ORR. EIS measurements were used in a wide frequency range and at different potentials from −0.50 to −0.05 V (vs. SCE) on copper in naturally aerated stagnant 0.5 M H₂SO₄. At the same time, the data were analyzed using appropriate equivalent circuits, and the influence of the anodic reaction was considered. Finally, kinetic information and the mechanism of the ORR were obtained, and a kinetic model describing the hump phenomenon was proposed. In contrast with that, some deaerated experiments were done to expect to confirm the propositional mechanism.

* Corresponding author. Tel.: +86 532 66782510; fax: +86 532 66782510.
E-mail address: xuwangri@163.com (H. Xu).

2. Experimental

The electrochemical measurements were conducted in a three-electrode cell at room temperature (20 °C) via a PowerSuite Electrochemical Interface. The working electrode was prepared from a polyurethane-coated copper wire. Prior to an experiment, the polycrystalline copper wire was dipped in a hot 98 wt% H₂SO₄ solution for several minutes to remove the coating, yielding a bare glassy pure copper wire (99.9%) with a diameter of 1.64 mm. Its tip and area around the water line were enclosed with paraffin to obtain a 4.48 cm² working area. The sample was finally cleaned in double-distilled water. The newly prepared electrode was then transferred immediately into the 200 ml electrochemical cell for reduction. A 10 cm² platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All potentials reported here are referred to the SCE.

In naturally aerated stagnant 0.5 M H₂SO₄, the copper electrode was held for 10 min at −0.70 V to reduce the surface oxide film and held for 10 min at −0.60 V to reach a steady current. Next, the potentiodynamic polarization curve was collected in the positive direction from −0.60 to 0.15 V at a scan rate of 0.166 mV s^{−1}. Before impedance measurements, the reduced (at −0.70 V) copper electrode was held to reach the stable state at given potentials from −0.50 to −0.05 V at 50 mV intervals.

In contrast, prior to measurements in deaerated stagnant 0.5 M H₂SO₄, the solution was purged with nitrogen (99.9%) for 1 h. Subsequently, a newly prepared copper electrode was inserted into the deaerated solution and held for 20 min at −0.65 V to reduce the surface oxide film. After that, bubbling gas was stopped, and the cell was enclosed. The polarization curve was collected from −0.50 to 0.15 V, and impedance measurements were performed at given potentials from −0.20 to −0.05 V at 50 mV intervals, as before.

All impedance experiments were done using AC signals with an amplitude of ±5 mV at 20 mHz–100 kHz range. A Solartron 1260 Frequency Response Analyzer and an EG&G PAR Model 273A Potentiostat/Galvanostat were used. Impedance data were fitted to appropriate equivalent circuits using Zview software.

3. Results and discussion

3.1. Polarization measurement

The potentiodynamic polarization curves in naturally aerated (solid line) and deaerated (dashed line) stagnant 0.5 M H₂SO₄ are shown in Fig. 1. In order to thoroughly consider the mechanism of the ORR on copper in naturally aerated stagnant 0.5 M H₂SO₄, we divided the cathodic part into three regions according to the different characteristics. Region I (−0.50 V < E < −0.40 V) refers to oxygen diffusion limiting current at high cathodic overpotentials; Region II (−0.40 V < E < −0.20 V) represents a mixed kinetic-diffusion control region; Region III (−0.20 V < E < −0.05 V) is defined as a hump phenomenon region where a maximum current density appears, which will be discussed in detail later. At potentials more negative than −0.50 V, the influence of the hydrogen evolution reaction (HER) cannot be neglected; discussion of this region is beyond the scope of this paper. The potential region more positive than −0.05 V is nearer to the corrosion potential, which relates to the complex anodic process and will be discussed in another paper.

In deaerated solution, the cathodic current density was largely reduced to less than 1 μA cm^{−2} in the wide range of the potential. In addition, the anodic dissolution rate was surprisingly reduced by the absence of the oxygen, compared with that in aerated solutions. Therefore, the acceleration of the cathodic reduction process on account of the oxygen is indicated, and the ORR mechanism will be discussed in detail below.

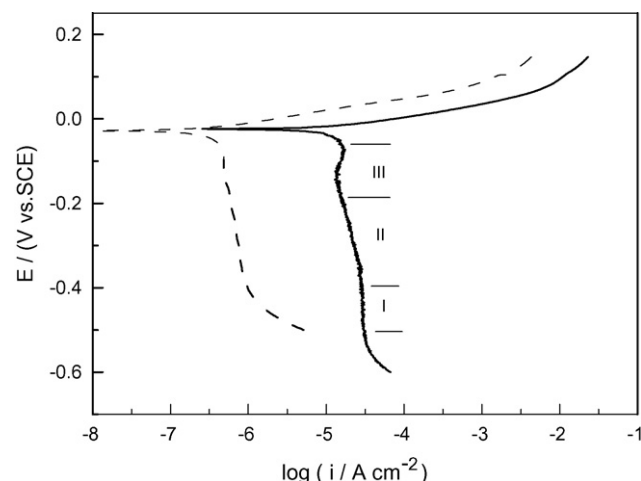


Fig. 1. Polarization curves on the positive going sweep on copper in naturally aerated (—) and deaerated (---) stagnant 0.5 M H₂SO₄. Scan rate: 0.166 mV s^{−1}. (I) The oxygen diffusion limiting current density region; (II) the mixed kinetic-diffusion controlled region; (III) the hump phenomenon region.

3.2. EIS measurements

3.2.1. ORR in Regions I and II

Regions I and II are the typical representatives of the ORR, and the impedance spectra are shown in Fig. 2a and b, respectively. A high-frequency capacitive loop and an obvious low-frequency diffusion characteristic were observed. The high-frequency capacitive loop is usually associated with the double layer charging–discharging process and rapid Faradaic capacitive process. The ORR is a complicated process that may generate certain types of intermediate reactive oxygen species, such as hydroxide, peroxide, superoxide, etc. Considering the low pH condition, here we simply categorize them into two kinds of reactions: the direct 2e[−]/4e[−] transfer step from oxygen molecules; and the reduction of the ORR intermediate species (e.g. H₂O₂, HO•, HO₂• and other medium valent species, etc.), which frequently adsorb to the surface [11] and will later be denoted as (HO_x)_{ads} for convenience. These two pathways are competitive in the ORR, with the latter requiring more negative potentials than the former, according to Zha [32].

The impedance spectra in Fig. 2a and b include experimental data, fitting curves, and the equivalent circuit. The fitted parameters are shown in Table 1. In the equivalent circuit, R_s represents solution resistance. Q is a constant phase element (CPE) substituting for the capacitive element to give a more accurate fit, whose admittance and impedance are expressed as [5,33]

$$Y = Y^0(j\omega)^n \quad (3)$$

and

$$Z = \left(\frac{1}{Y^0} \right) (j\omega)^{-n} \quad (4)$$

Table 1

Impedance parameters of copper at −0.50 to −0.20 V (vs. SCE) in naturally aerated stagnant 0.5 M H₂SO₄.

E (V)	R _s (Ω cm ²)	Y _{dl} ⁰ (μF cm ^{−2})	n _{dl}	R _{O-ads} (Ω cm ²)	R _{t-O2} (Ω cm ²)	1/Y _w ⁰ (Ω cm ²)
−0.50	1.68	65.48	0.93	24,572	2966	10347.68
−0.45	1.68	57.35	0.94	17,003	3433	8372.40
−0.40	1.68	53.74	0.94	13,034	3858	8650.52
−0.35	1.68	51.48	0.95	13,548	3936	7236.94
−0.30	1.68	51.03	0.95	15,462	4460	5241.36
−0.25	1.68	53.06	0.94	18,845	5040	3110.23
−0.20	1.68	57.35	0.94	19,891	6555	2339.67

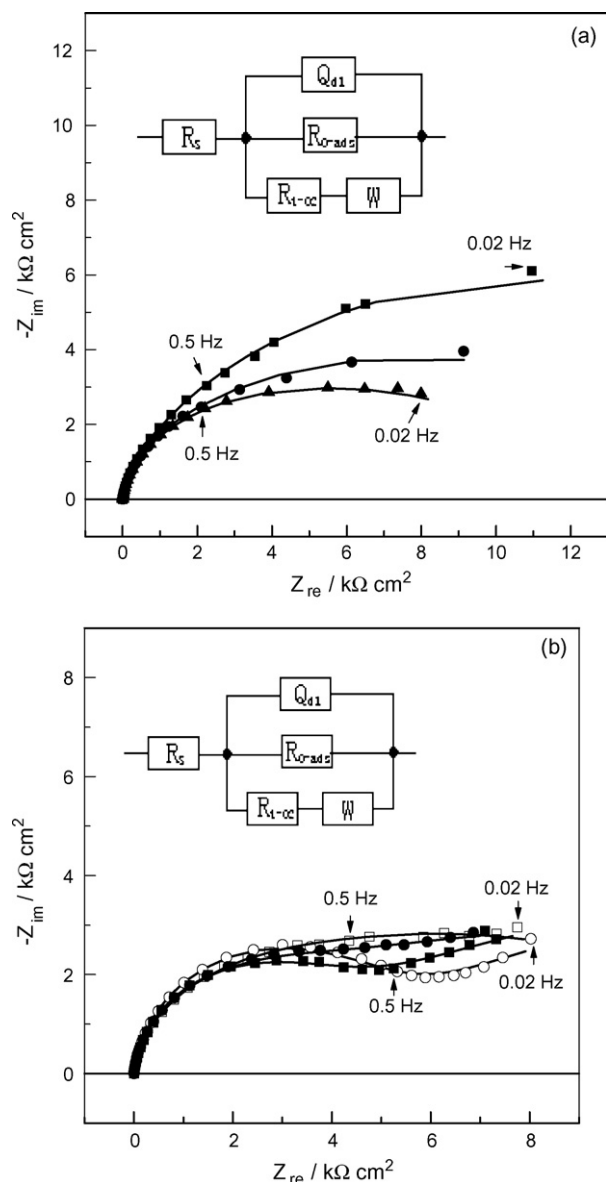


Fig. 2. Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in naturally aerated stagnant 0.5 M H₂SO₄ at different potentials (vs. SCE). (a) –0.50 V (■); –0.45 V (●); –0.40 V (▲); –0.35 V (□); –0.30 V (○); –0.25 V (■); –0.20 V (●). The insert is the equivalent circuit model.

where Y^0 is the magnitude of Q , ω the angular frequency, and n the exponential term relating to the roughness of electrode surface. R_{O-ads} is the charge-transfer resistance of further reduction of the aforementioned adsorbed intermediates. R_{t-O_2} is the charge-transfer resistance of the direct $2e^-/4e^-$ ORR from oxygen molecules. W is the Warburg impedance, which is equivalent to Q when $n = 0.5$, and Q is equivalent to a capacitance when $n = 1$ and to inductance when $n = -1$. The subscript dl denotes the electric double layer, and w denotes the Warburg impedance. In Table 1, the value of Y_{dl}^0 is less than $100 \mu F cm^{-2}$, and n_{dl} is nearly equal to 1; therefore Q_{dl} in the equivalent circuit can simply be regarded as pure capacitance and replaced with C_{dl} in literature [5,34]. $1/Y_w^0$ is the magnitude of the Warburg impedance, i.e., the oxygen diffusion from the bulk solution to electrode surface.

From Table 1, $R_{t-O_2} \ll R_{O-ads}$; they are parallel in the equivalent circuit (see the insert in Fig. 2a), indicating that the direct $2e^-/4e^-$ ORR is a fast step and has greater influence on the cathodic process; therefore, it is the step we primarily consider. Moreover, $1/Y_w^0 \gg$

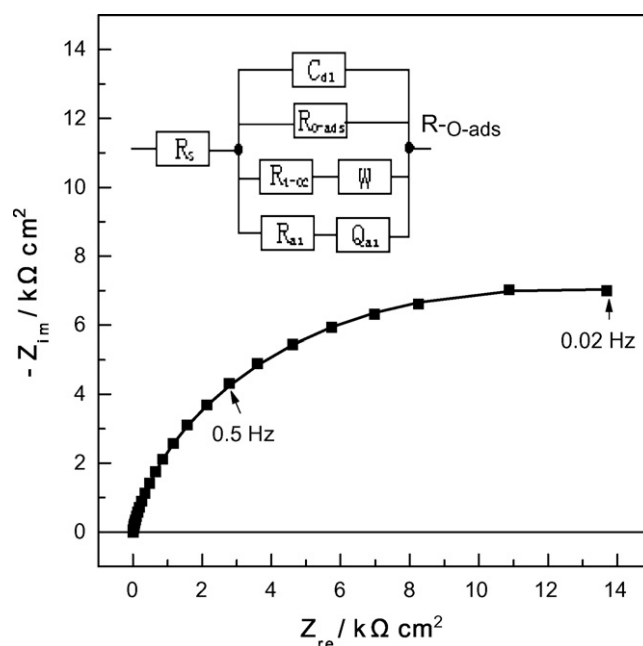


Fig. 3. Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in naturally aerated stagnant 0.5 M H₂SO₄ at –0.15 V (vs. SCE). The insert is the equivalent circuit model.

R_{t-O_2} , indicating that the direct $2e^-/4e^-$ ORR is controlled by oxygen diffusion in Region I ($-0.50 V < E < -0.40 V$). Vukmirovic et al. [35] concluded that the $4e^-$ oxygen reduction of copper occurred in naturally aerated 0.1 M Na₂SO₄ (pH 1.5–14), and diffusion-limited current density (i_L) was $20\text{--}30 \mu A cm^{-2}$ independent of pH, while we obtained $i_L \approx 30 \mu A cm^{-2}$ in our experiments. Wilms et al. [17] investigated specific anion adsorption on Cu(111) in H₂SO₄ and found desorption at potentials more negative than ca. $-0.35 V$ (vs. SCE). Jiang and Brisard [4] indicated that the major effect of the anions on Cu(*hkl*) surfaces was the blocking of active sites for the co-adsorption of oxygen molecules. As a result, the desorption of anions in Region I increases the available active area of the copper surface, which may facilitate co-adsorption and breakage of the O–O bond of oxygen molecules, leading to dominance of the $4e^-$ pathway.

In Region II ($-0.40 V < E < -0.20 V$), cathodic current density decreases as the potential becomes less negative (see Fig. 1), and the low-frequency diffusion characteristic weakens as shown in Fig. 2b. The charge-transfer resistances, R_{O-ads} and R_{t-O_2} , increase while $1/Y_w^0$ decreases (see Table 1), until $1/Y_w^0 < R_{t-O_2}$. Therefore, a combined kinetic-diffusion control process appears. There is a local increase in diffusion rate at the electrode surface and the adsorption of large amount of (bi)sulfate anions will inhibit the co-adsorption and the breakage of O–O bond of oxygen molecules. Obviously, a $4e^-$ pathway will be inhibited while a $2e^-$ pathway is facilitated. The increases in R_{O-ads} and R_{t-O_2} are attributed to a reduced electrochemical drive due to lower cathodic overpotentials. Coupled with an increase in $2e^-$ transfers relative to $4e^-$ owing to the adsorption of (bi)sulfate anion, this adequately explains the decrease of the cathodic current density in this region.

3.2.2. Hump phenomenon in Region III

Region III ($-0.20 V < E < -0.05 V$) is a complicated and distinctive region. From Fig. 1, the current density reaches a minimum at ca. $-0.15 V$ and then increases with potential, reaching a maximum at ca. $-0.05 V$. Meanwhile, a low-frequency capacitive loop at $-0.15 V$, a second phase spectrum at $-0.10 V$ and low-frequency diffusion at $-0.05 V$ appear in the impedance diagrams. These are presented in

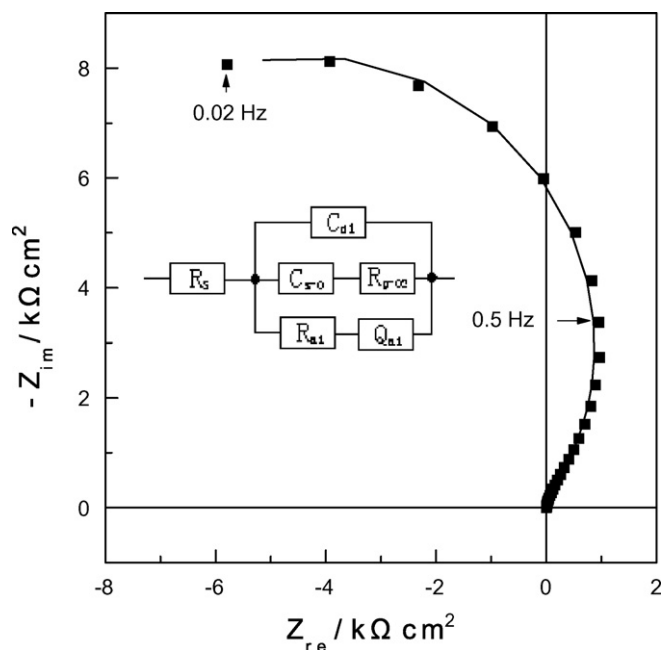


Fig. 4. Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in naturally aerated stagnant 0.5 M H₂SO₄ at –0.10 V (vs. SCE). The insert is the equivalent circuit model.

Figs. 3–5, respectively, and the related impedance parameters are listed in Tables 2–4, respectively.

Ghandehari et al. [12] attributed this phenomenon to the inhibition of the ORR by a cathodic film composed of the ORR intermediates and adsorbed sulfate anions, which was able to be removed by rapid dissolution of the substrate copper. On the other hand, Schultze and Wippermann [22] explained it as the electro-deposition (cathodic reduction) of the copper cation; however, it seems impossible for this occur on a freshly reduced copper surface at any significant rate. It seems reasonable to include anodic reaction in Region III at low cathodic overpotentials in light of Ghandehari et al. [12].

The anodic dissolution at low overpotentials involves the following reactions [36–40]:

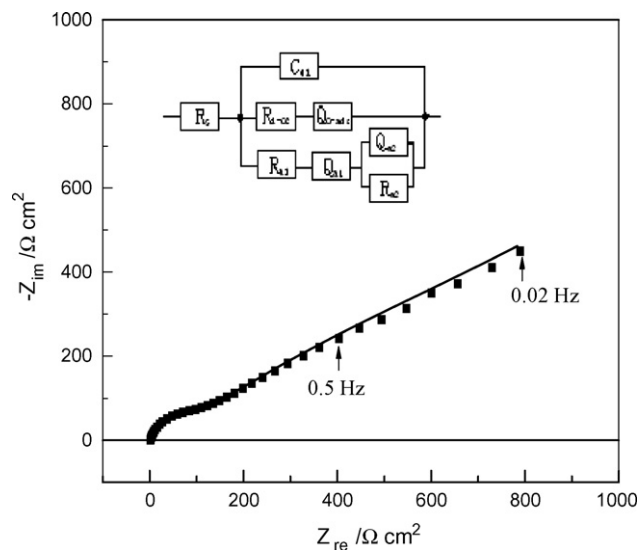
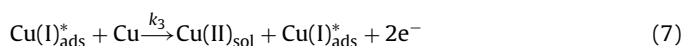


Fig. 5. Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in naturally aerated stagnant 0.5 M H₂SO₄ at –0.05 V (vs. SCE). The insert is the equivalent circuit model.



where the Cu(I)_{ads} is an adsorbed monovalent species of copper at the electrode surface. According to Cordeiro et al. [37], the Cu(I)_{ads} may transform further into a new interfacial species, Cu(I)_{ads}^{*} (monovalent species) (Eq. (6)). Cu(I)_{ads}^{*} is another dissolution intermediate species and plays a catalytic role; i.e., Eq. (7) is usually an autocatalytic reaction. Furthermore, Cu(I)_{ads}^{*} is considered likely to be (bi)sulfate anion-associated (have (bi)sulfate incorporated into its structure); Wong et al. [38] suggested that it can be desorbed from the electrode surface and diffuse into the bulk solution.

For the corrosion of copper in oxygenated H₂SO₄, Andersen et al. [23] proposed an explanation of the chemical attack by dissolved oxygen on cuprous ions. At the same time, Vazquez et al. [14,15] suggested that the electrochemical reduction of H₂O₂ on copper in a borax buffer is catalyzed by a redox cycle involving the Cu(I)/Cu(II) couple.

Considering the involvement of the anodic reactions and the possible catalysis effect of the cuprous species, a coupled electrochemical/chemical process (the EC mechanism) in the hump phenomenon region was proposed as follows:

Table 2
Impedance parameters of copper at –0.15 V (vs. SCE) in naturally aerated stagnant 0.5 M H₂SO₄.

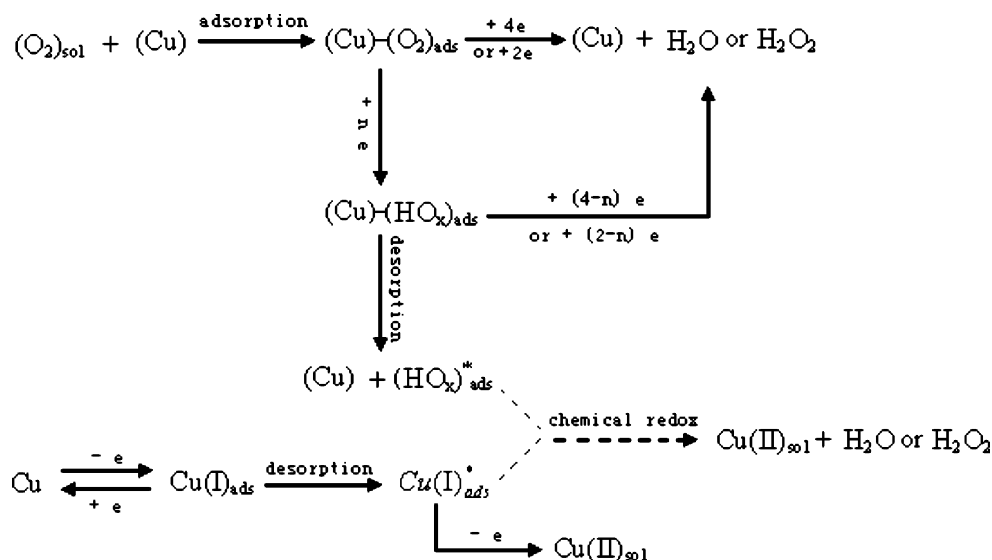
E (V)	R _s (Ω cm ²)	C _{dl} (μF cm ^{–2})	R _{O-ads} (Ω cm ²)	R _{t-O2} (Ω cm ²)	1/Y _w ⁰ (Ω cm ²)	R _{a1} (Ω cm ²)	1/Y _{a1} ⁰ (Ω cm ²)	n _{a1}
–0.15	1.77	33.65	34,418	25,307	9544.72	35.93	16051.3	0.70

Table 3
Impedance parameters of copper at –0.10 V (vs. SCE) in naturally aerated stagnant 0.5 M H₂SO₄.

E (V)	R _s (Ω cm ²)	C _{dl} (μF cm ^{–2})	C _{s-o} (F cm ^{–2})	R _{p-o2} (Ω cm ²)	R _{a1} (Ω cm ²)	1/Y _{a1} ⁰ (Ω cm ²)	n _{a1}
–0.10	1.87	37.42	0.014	–7826	25.69	4287.1	0.53

Table 4
Impedance parameters of copper at –0.05 V (vs. SCE) in naturally aerated stagnant 0.5 M H₂SO₄.

E (V)	R _s (Ω cm ²)	C _{dl} (μF cm ^{–2})	R _{t-O2} (Ω cm ²)	1/Y _{O-ads} ⁰ (Ω cm ²)	n _{O-ads}	R _{a1} (Ω cm ²)	1/Y _{a1} ⁰ (Ω cm ²)	n _{a1}	Y _{a2} ⁰ (μF cm ^{–2})	n _{a2}	R _{a2} (Ω cm ²)
–0.05	1.94	37.8	1440.3	259.6	0.50	16.1	615.0	0.52	145.4	0.80	73.7



The anodic dissolution reaction in Eq. (5) is a fast step, and the reaction rates of Eqs. (6) and (7) depend on the potentials. Therefore, the anodic reactions take place near the corrosion potential, at which point the two intermediates, $\text{Cu}(\text{I})_{\text{ads}}$ and $\text{Cu}(\text{I})_{\text{ads}}^*$, may appear. The anodic process elements R_{a1} and Q_{a1} are added into the equivalent circuits in Figs. 3 and 4. R_{a1} represents the charge transfer resistance from Cu to $\text{Cu}(\text{I})_{\text{ads}}$. The constant phase element Q_{a1} indicates that $\text{Cu}(\text{I})_{\text{ads}}$ desorbs from the surface and diffuses into the double layer to form $\text{Cu}(\text{I})_{\text{ads}}^*$. The physical meanings of R_s , $R_{\text{O-ads}}$, $R_{\text{t-O2}}$ and W are the same as those expressed in the equivalent circuit of Fig. 2.

At -0.15 V, $R_{\text{O-ads}}$ and $R_{\text{t-O2}}$ significantly increase (see Table 2); the latter in particular is a factor of four times greater than that at -0.20 V. Both reach a nearly comparable resistance, indicating that both ORR pathways are significantly inhibited and have nearly equal influence on the ORR. This may be due to the presence of more intermediate species and adsorbed (bi)sulfate anions. A characteristic of drastic increase of impedance $1/Y_{\text{w}}^0$ arises, with a value nearly approaching those when i_L appears in Region I, indicating a significant deceleration of the oxygen diffusion rate. This slow oxygen diffusion may be due to competition for adsorption sites with oxygen molecules, the intermediate species, and (bi)sulfate anions. Though the anodic reaction resistance R_{a1} is small, it is controlled by large $1/Y_{a1}^0$, and therefore the large $R_{\text{O-ads}}$, $R_{\text{t-O2}}$ and $1/Y_{a1}^0$ together result in the minimum current density.

At -0.1 V, a second phase impedance spectrum with the equivalent circuit is shown in Fig. 4 and a simultaneous increase in the current density appears (see solid line in Fig. 1). This is analogous to the “dissolution → passivation” transition characteristic in the anodic passivation phenomenon. Cao and Zhang [33] indicated that the second phase impedance will appear when the polarization current decreases with increasing polarization potential. However, this is seldom observed in the cathodic potential region. In the equivalent circuit of Fig. 4, the cathodic process elements discussed above are replaced by capacitance $C_{\text{s-O}}$ and resistance $R_{\text{p-O2}}$. The negative resistance $R_{\text{p-O2}}$ is attributed to the polarization resistance of the ORR (because the charge-transfer resistance must be positive, $R_{\text{p-O2}}$ is therefore the combination of a negative resistance and a positive charge-transfer resistance). The large capacitance $C_{\text{s-O}}$ is not simply the double layer capacitance but may correspond to the desorption of the ORR intermediates.

Eq. (6) is the rate-limiting step in the overall anodic reactions at -0.15 and -0.10 V, judging from the values of $1/Y_{a1}^0$ and n_{a1} in Tables 2 and 3. Meanwhile, the decreases of R_{a1} and $1/Y_{a1}^0$ imply the

acceleration of the anodic reaction as the potential becomes more positive.

The abnormal increase of cathodic current density indicates an acceleration of the ORR, although the negative $R_{\text{p-O2}}$ cannot provide us with additional information. One possible explanation for this is that the adsorbed sulfate anions are removed easily with the desorption and diffusion of $\text{Cu}(\text{I})_{\text{ads}}$, and as a result more fresh electrode surface is exposed for the ORR. However, this may play only a minor role, since the proportion of anodic reaction increases at more positive potentials. On the other hand, the major reason may be the chemical redox between $\text{Cu}(\text{I})_{\text{ads}}^*$ and the desorbed ORR intermediates $(\text{HO}_x)_{\text{ads}}$ (i.e., $(\text{HO}_x)_{\text{ads}}^*$) in the double layer (see the EC mechanism). The above mechanisms would lead to easier diffusion and adsorption of oxygen molecules towards the surface, i.e., the decrease of the diffusion resistance, and hence, the diffusion element is not included in the equivalent circuit of Fig. 4.

At -0.05 V, the impedance spectrum and the equivalent circuit are shown in Fig. 5. The impedance parameters are listed in Table 4, where $R_{\text{t-O2}}$ and $Q_{\text{O-ads}}$ represent the cathodic equivalent elements, whereas R_{a1} , Q_{a1} , Q_{a2} , and R_{a2} are anodic ones, which will be explained later. A potential-current density peak appears in Fig. 1 and the current density is about $15 \mu\text{A cm}^{-2}$, which is near the corrosion rate and indicates an influence on it [39]. At medium and low frequencies, the second phase impedance disappears, and diffusion characteristics appear (see Fig. 5). This behavior may correspond to the diffusion of the desorbed ORR intermediates and the mass transfer of cuprous species towards the double layer, which is consistent with the values of $n_{\text{O-ads}}$ and n_{a1} (nearly 0.5). Compared with those at more negative potentials, $R_{\text{t-O2}}$ in Table 4 decreased greatly, indicating that the ORR mechanism changed due to the coupled electrochemical/chemical process. Thereby $R_{\text{t-O2}}$ in the equivalent circuit of Fig. 5 represents the charge-transfer resistance of forming the ORR intermediates $(\text{HO}_x)_{\text{ads}}$ from the reduction of oxygen molecules, $Q_{\text{O-ads}}$ represents the diffusion of the desorbed $(\text{HO}_x)_{\text{ads}}$ towards the double layer to form $(\text{HO}_x)_{\text{ads}}^*$, an ORR intermediate and probably cation-associated, which can be desorbed and diffuse into the bulk solution. The former determines the latter from $R_{\text{t-O2}} \gg 1/Y_{\text{O-ads}}^0$; i.e., the electrochemical reaction is a slower step compared with the diffusion process. Finally, the acceleration of the ORR is indicated by the small $R_{\text{t-O2}}$ (referring to the electrochemical reduction) and $1/Y_{\text{O-ads}}^0$ (referring to the chemical reduction). That is to say, the rate of electrochemical reduction determines that of the chemical reduction and the latter similarly promotes the former; i.e., the synergetic effect accelerates the ORR.

Table 5
Impedance parameters of copper at -0.20 to -0.05 V (vs. SCE) in deaerated stagnant 0.5 M H_2SO_4 .

E (V)	R_s ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	R_{t-O_2} ($\text{k}\Omega \text{ cm}^2$)	$1/Y_w^0$ ($\text{k}\Omega \text{ cm}^2$)	R_{a1} ($\Omega \text{ cm}^2$)	Y_{a1}^0 ($\mu\text{F cm}^{-2}$)	n_{a1}
-0.20	1.33	48.24	96.16	12.79	–	–	–
-0.15	1.31	50.98	97.75	14.8	–	–	–
-0.10	1.35	31.83	56.91	35.40	30.87	35.5	0.79
-0.05	1.35	36.02	19.88	6.96	21.42	48.07	0.79

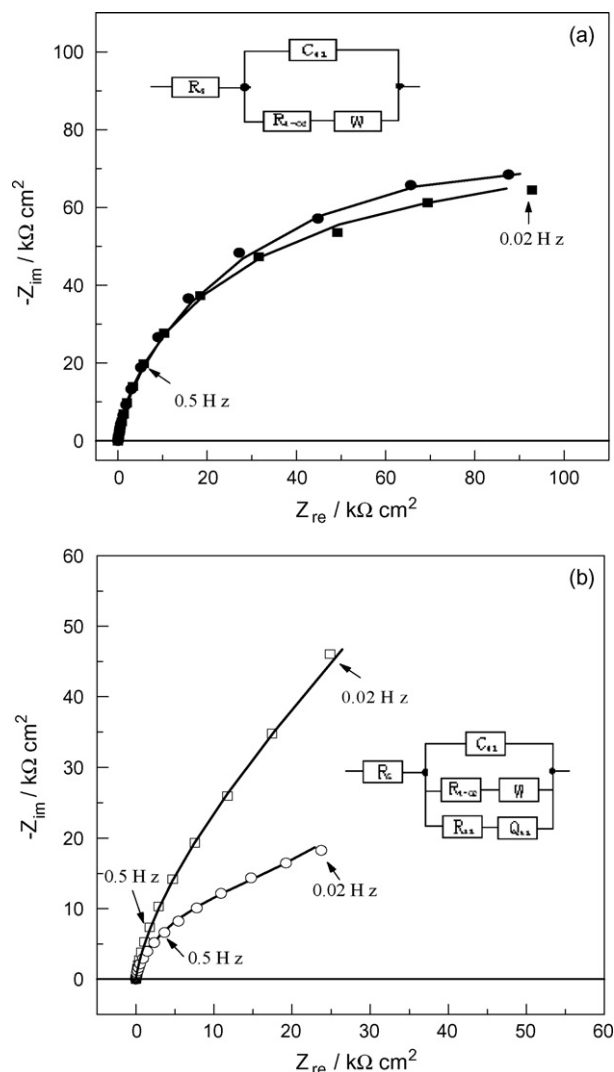


Fig. 6. Nyquist impedance spectra for the fit (line) and experimental data (symbol) on copper in deaerated stagnant 0.5 M H_2SO_4 at different potentials. (a) -0.20 V (■) and -0.15 V (●); (b) -0.10 V (□) and -0.05 V (○) (vs. SCE). The insert is the equivalent circuit model.

The anodic reaction rate in Eq. (7) on copper cannot be neglected at -0.05 V (which is closer to the corrosion potential). Two new anodic process elements R_{a2} and Q_{a2} are added. The former is the charge-transfer resistance to form $\text{Cu(II)}_{\text{sol}}$ and the latter is the parallel constant phase element of the former, resembling a capacitance from $n=0.8$. The anodic reaction rate in Eq. (7) is proved slower than that in Eq. (5) by the larger values of R_{a2} . Moreover, $1/Y_{a1}^0 \gg R_{a1}$ and R_{a2} ; as a result, the anodic dissolution of copper is controlled by the mass transfer of $\text{Cu(I)}_{\text{ads}}$, and the chemical and electrochemical oxidation processes occur simultaneously.

3.2.3. Hump phenomenon in deaerated stagnant 0.5 M H_2SO_4

In order to clarify the EC mechanism in the hump phenomenon region, the impedance measurements were done in deaerated stag-

nant 0.5 M H_2SO_4 . The impedance spectra and equivalent circuits are presented in Fig. 6a (at -0.20 and -0.15 V) and Fig. 6b (at -0.10 and -0.05 V), and the related impedance parameters are listed in Table 5.

R_{t-O_2} is the charge-transfer resistance of the direct $2e^-/4e^-$ ORR from oxygen molecules. W is the Warburg impedance. From Table 5, R_{t-O_2} is much larger than that in naturally aerated solution, which results in the decrease of the ORR current density on polarization curve (dashed line in Fig. 1), and the delay of the presence of the anodic reactions at more positive potentials (up to -0.10 V). R_{a1} represents the charge transfer resistance from Cu to $\text{Cu(I)}_{\text{ads}}$, which is approximately equal to those in naturally aerated solution. However, it is noticeable that no second phase impedance spectrum appears at -0.1 V. Even though the anodic reactions are present, the absence of the ORR intermediates makes the chemical redox difficult to occur and, consequently, renders the hump phenomenon indistinctive (see dashed line in Fig. 1) consequently.

Here, the constant phase element Q_{a1} is no longer related to the diffusion behavior; instead, it resembles the capacitance from its n (nearly 0.8). It is difficult for $\text{Cu(I)}_{\text{ads}}$ to diffuse into the solution, even at -0.05 V. As the potential becomes more positive, more $\text{Cu(I)}_{\text{ads}}$ absorbs at the electrode surface; thus, Y_{a1} increases. On the other hand, in naturally aerated solution, Q_{a1} relates to the diffusion of the cuprous ions, which can be oxidized into the cupric ions.

By comparing the deaerated experiments with the aerated ones, the hump phenomenon can be thoroughly explained. The stable presence of the ORR intermediates enables chemical redox by coupling with the anodic dissolution intermediates. Therefore, the EC mechanism is proved reasonable, as expected.

4. Conclusion

The mechanisms of the cathodic ORR were investigated in a naturally aerated stagnant 0.5 M H_2SO_4 : (1) The main process involved $4e^-$ process controlled by diffusion at -0.50 to -0.40 V; (2) A combined kinetic-diffusion controlled process appears at -0.40 to -0.20 V, with a $2e^-$ transfer instead of $4e^-$ due to the adsorption of the (bi)sulfate anion; (3) A hump phenomenon appears at -0.20 to -0.05 V, and a synergistic EC mechanism is proposed; i.e., the chemical redox between the anodic intermediate $\text{Cu(I)}_{\text{ads}}$ and the ORR intermediates $(\text{HO}_x)_{\text{ads}}^*$, coupled with the electrochemical reactions, synergistically results in the increase of the ORR. Moreover, close to the corrosion potential, the overall anodic reactions are controlled by the mass transfer of the cuprous species, whereas the cathodic ones are controlled by the kinetic process.

The fitted results are in good agreement with the experimental ones. Furthermore, the EC mechanism is confirmed by the deaerated experiments.

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References

- [1] J. Reid, *Jpn. J. Appl. Phys.* 40 (2001) 2650.
- [2] F.A. Lowenheim, *Modern Electroplating*, John Wiley and Sons, New York, 1974, p. 636.
- [3] A.G. Zelinsky, B.Ya. Pirogov, O.A. Yurjev, *Corros. Sci.* 46 (2004) 1083.
- [4] T. Jiang, G.M. Brisard, *Electrochim. Acta* 52 (2007) 4487.
- [5] H.Y. Ma, S.H. Chen, B.S. Yin, S.Y. Zhao, X.Q. Liu, *Corros. Sci.* 45 (2003) 867.
- [6] G. Brisard, E. Zenati, H.A. Gasteiger, N.M. Marković, P.N. Ross, *Langmuir* 13 (1997) 2390.
- [7] G. Brisard, N. Bertrand, P.N. Ross, N.M. Marković, *J. Electroanal. Chem.* 480 (2000) 219.
- [8] V.N. Vesovic, N. Anastasijevic, R.R. Adzic, *J. Electroanal. Chem.* 218 (1987) 53.
- [9] D. Wayne Suggs, A.J. Bard, *J. Phys. Chem.* 99 (1995) 8349.
- [10] D. Pletcher, S. Sotiropoulos, *J. Electroanal. Chem.* 356 (1993) 109.
- [11] E. Yeager, *Electrochim. Acta* 29 (1984) 1527.
- [12] M.H. Ghandehari, T.N. Andersen, H. Eyring, *Corros. Sci.* 16 (1976) 123.
- [13] E.J. Calvo, D.J. Schiffrin, *J. Electroanal. Chem.* 243 (1988) 171.
- [14] M.V. Vazquez, S.R. de Sanchez, E.J. Calvo, D.J. Schiffrin, *J. Electroanal. Chem.* 374 (1994) 179.
- [15] M.V. Vazquez, S.R. de Sanchez, E.J. Calvo, D.J. Schiffrin, *J. Electroanal. Chem.* 374 (1994) 189.
- [16] F. King, M.J. Quinn, C.D. Litke, *J. Electroanal. Chem.* 385 (1995) 45.
- [17] M. Wilms, P. Broekmann, M. Kruff, Z. Park, C. Stuhlmann, K. Wandelt, *Surf. Sci.* 402–404 (1998) 83.
- [18] G.M. Brown, G.A. Hope, *J. Electroanal. Chem.* 382 (1995) 179.
- [19] M. Wilms, P. Broekmann, C. Stuhlmann, K. Wandelt, *Surf. Sci.* 416 (1998) 121.
- [20] D.P. Schweinsberg, S.E. Bottle, V. Otieno-Alego, *J. Appl. Electrochem.* 27 (1997) 161.
- [21] J.O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 2, Plenum Press, New York, 1972, p. 706.
- [22] J.W. Schultze, K. Wippermann, *Electrochim. Acta* 32 (1987) 823.
- [23] T.N. Andersen, M.H. Ghandehari, H. Eyring, *J. Electrochem. Soc.* 122 (1975) 1580.
- [24] H.Y. Ma, S.H. Chen, S.Y. Zhao, X.Q. Liu, D.G. Li, *J. Electrochem. Soc.* 148 (2001) B482.
- [25] O.E. Barcia, O.R. Mattos, *Electrochim. Acta* 35 (1990) 1601.
- [26] M.R.F. Hurtado, P.T.A. Sumodjo, A.V. Benedetti, *Electrochim. Acta* 48 (2003) 2791.
- [27] J.D. Reid, A.P. David, *J. Electrochem. Soc.* 134 (1987) 1389.
- [28] Y.L. Cheng, Z. Zhang, F.H. Cao, J.F. Li, J.Q. Zhang, J.M. Wang, C.N. Cao, *Corros. Sci.* 46 (2004) 1649.
- [29] D.B. Zhou, H.V. Poorten, *Electrochim. Acta* 40 (1995) 1819.
- [30] J.B. Matos, L.P. Pereira, S.M.L. Agostinbo, O.E. Barcia, G.G.O. Cordeiro, E. D'Elia, *J. Electroanal. Chem.* 570 (2004) 91.
- [31] D.D. Macdonald, *Transient Techniques in Electrochemistry*, Plenum Press, New York, 1977, p. 229.
- [32] Q.X. Zha, *Introduction to Kinetics of Electrode Processes*, Science Press, Beijing, 2002, p. 74.
- [33] C.N. Cao, J.Q. Zhang, *Introduction to Electrochemical Impedance Spectroscopy*, Science Press, Beijing, 2002, p. 45.
- [34] A.J. Bard, L.R. Faulkner, in: Y.H. Shao, G.Y. Zhu, X.D. Dong, B.L. Zhang (Eds.), *Electrochemical Methods*, Chemical Industry Press, Beijing, 2005, p. 373.
- [35] M.B. Vukmirovic, N. Vasiljevic, N. Dimitrov, K. Sieradzki, *J. Electrochem. Soc.* 150 (2003) B10.
- [36] E. Mattson, J.O'M Bockris, *Trans. Faraday Soc.* 58 (1962) 1586.
- [37] G.G.O. Cordeiro, O.E. Barcia, O.R. Mattos, *Electrochim. Acta* 38 (1993) 319.
- [38] D.K.Y. Wong, B.A.W. Coller, D.R. MacFarlane, *Electrochim. Acta* 38 (1993) 2121.
- [39] G. Moretti, F. Guidi, *Corros. Sci.* 44 (2002) 1995.
- [40] A.H. Moreira, A.V. Benedetti, P.L. Cabot, P.T. Sumodjo, *Electrochim. Acta* 38 (1993) 981.