Oxygen reduction reaction kinetics on pure copper in neutral sodium sulfate solution

Nisrine Benzbiria¹ · Mustapha Zertoubi¹ · Mohammed Azzi¹

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Abstract

Oxygen reduction reaction (ORR) kinetics were investigated on different copper surface conditions in 10^{-2} M Na_2SO_4 solution. On pre-reduced and passivated copper surfaces, the ORR is suggested to occur by a parallel pathway involving HO_2^- formation followed by its diffusion to the solution or rapid reduction to OH^- . A significant difference in ORR activity is observed in the kinetic and mixed control regions as copper surface becomes more oxidized. On a surface covered by ammonium pyrrolidine dithiocarbamate (PDTC), ORR rate is inhibited due to the adsorption of PDTC and formation of a protective film, which limits O_2 deposition on copper surface regardless of pH values and oxygen concentration in the solution.

Keywords Oxygen reduction reaction · Copper · Na_2SO_4 · Electrochemical methods · SEM/EDX · XRD

1 Introduction

Oxygen reduction reaction (ORR) is one of the most widely investigated electrochemical reactions due to its interest in energy conversion systems from metal/air batteries [1, 2] and fuel cells [3, 4]. Considerable works have been devoted to study the kinetics, mechanism and the effect of ORR electrocatalysts over the past years. Platinum- and palladium-based metals are still considered the best electrocatalysts for ORR [5–8], but these metals are costly and have limited availability on earth. To reduce catalyst cost and improve ORR activity, alloying noble metals with other metals [9–12], such as cobalt, iron and copper show a remarkable synergistic catalytic effect. That being said, electrocatalysts including copper have attracted attention and were extensively used on non-platinum catalysts due to noticeable selectivity to oxygen reduction and reasonable activity [2, 10, 11, 13–16].

Numerous reaction mechanisms have been suggested to outline ORR in aqueous solutions [17, 18]. Among

others, the model presented in Fig. 1 is utmost employed because of its pertinence over a large potential domain [19].

In alkaline and neutral solutions, this model summarizes ORR as a multi-electron process that can occur through two main courses: a direct four-electron reduction to OH^- following Eq. (1) [20] or an indirect reduction involving the formation of intermediates such as HO_2^- through a two electron pathway, which may undergo additional reduction or decomposition by Eqs. (2) and (3) [21].

ORR proceeding via reactions (2) and (3) is considered a serial mechanism, while the reduction following reactions (1) and (2–3) is called parallel mechanism [22].

✉ Nisrine Benzbiria, nisrine.benzbiria@gmail.com | ¹Laboratory of Interface Materials Environment, Faculty of Sciences Aïn Chock, Hassan II University of Casablanca, Casablanca, Morocco.

Fig. 1 Simplified scheme of possible paths of oxygen reduction reaction (ORR) [19]

In fact, several factors have a crucial effect on the reduction pathway, such as the presence of adsorbing species (Cl^- , SO_4^{2-} ...), O_2 level and specifically the surface condition of the studied metal [20, 23–26]. Besides, ORR mechanism becomes more complicated if it occurs on non-noble metals where the formation of the oxide layers is involved [27, 28]. Indeed, these metals interact with oxygen dissolved in the solution to form intermediates species in ORR process. Accordingly, earlier studies claimed that ORR rate is slower on oxidized surfaces than on bare electrodes [21, 27, 29–31].

To date, most of the significant work in this field was aimed at studying the catalytic activity of Pt(hkl) toward O_2 reduction process by a rotating ring–disk electrode (RRDE) configuration, while existing results for ORR on copper are considered to be few. The previous studies on copper suggested a four-electron pathway mechanism involving the effect of the metal oxidation state on the reaction kinetics [20, 23–25, 27, 32–34]. For instance, in supersaturated 0.1 M borax buffer solution, Vazquez et al. [27] found that metal oxidation to $\text{Cu}/\text{CuO}/\text{Cu}_2\text{O}$ duplex layer lowered copper catalytic activity. They stated that Cu_2O was considered to act as a barrier film [27]. The authors also suggested that ORR proceeds by both a chemical–electrochemical (CE) mechanism and a four-electron pathway. King et al. [24] claimed as well that a complete coverage of the surface by Cu_2O monolayer inhibited ORR in 1 mol dm^{-3} NaCl, while a partial reduction in Cu_2O monolayer was found to enhance ORR rate.

The influence of adsorbed anions existing in the solution was also reported [23, 25, 27, 32, 34]. According to Balakrishnan [25], the anion effect is altered depending on its impact on both cathodic and anodic reactions. It has been proposed that oxygen reduction in Na_2SO_4 solution occurs through parallel steps, one entailing direct reduction to H_2O or OH^- , while the alternative step involves the formation of stable H_2O_2 [25]. Vazquez et al. [27], who added NH_4Cl to the solution as a complexing agent capable of dissolving Cu_2O , reported that peroxide reduction was inhibited in the potential range investigated and a rate increase was observed. Yonghong Lu et al. [32] studies in 0.5 M H_2SO_4 medium suggested that ORR induced three

regions: firstly, a potential region controlled by diffusion including a limiting current density where ORR occurred through the main transfer of four electrons, secondly a combined kinetic diffusion region with a supplementary two electron pathway related to bisulfate anion adsorption and finally the region of a hump phenomenon, where the anodic intermediate $\text{Cu(I)}_{\text{ads}}^*$ reacted with oxygen reduction intermediates $(\text{HOx})_{\text{ads}}^*$, which led to ORR enhancement in a synergic way. In a similar way, Brisard et al. [23] stated that the nature of the adsorbates had a strong influence on the ORR mechanism. As a matter of fact, O_2 reduction on copper in 0.1 M HClO_4 solution generated a two electron transfer at low cathodic potentials due to the adsorption of oxygenated species, while the current plateau depicted a direct electron transfer at high negative potential region. Otherwise, ORR kinetics were under mixed control process in 0.5 M H_2SO_4 medium. The authors reported that bisulfate anions blocked active copper sites for the adsorption of oxygen molecules, which had a main influence on ORR kinetics and reaction pathway [23].

Yet, oxygen reduction has not been investigated in depth by means of neither experimental methods dedicated to describe surface electrochemistry, nor theoretical studies. As an example, relatively few studies have used the electrochemical impedance spectroscopy (EIS) as a tool to reveal the ORR mechanisms [32, 35–37].

In the current work, the kinetics of oxygen reduction reaction in 10^{-2} M Na_2SO_4 are investigated on copper surfaces exposed to different pre-treatments (pre-reduction, passivation and modification with PDTC molecule). No such detailed study seems to be conducted on copper. After pre-treatments, copper surface was characterized by SEM images coupled with EDX analysis and XRD. A rotating disk electrode (RDE) was utilized to study the influence of electrode rotation rate, and the kinetic parameters were determined using the Koutecky–Levich treatment. Then, to give further insights into the oxygen reduction process, EIS experiments were carried out at various cathodic potentials where ORR is believed to be the principal cathodic reaction.

2 Experimental

2.1 Electrode preparation and conditions

Experiments were performed with a 99.999% copper cylindrical rod having a diameter of 5 mm. Before the experiments, copper electrode was mechanically polished with SiC papers with a particle grade of 1200, washed with distilled water and then immediately transferred to the cell. Each experiment was performed on a freshly prepared

electrode. The study was conducted on three surface conditions:

- (1) Pre-reduced surface: The polished surface was exposed to a cathodic polarization of -1.3 V/saturated calomel electrode (SCE) for 3 min, in the working electrolyte itself [27].
- (2) Passivated surface: An anodic polarization at $+400$ mV/SCE was held on the specimens for one hour in an aerated borate buffered electrolyte (10^{-2} M $\text{H}_3\text{BO}_3 + 10^{-2}$ M $\text{Na}_2\text{B}_4\text{O}_7$; pH = 9) [38].
- (3) Surface covered with PDTC: After polishing the electrode, copper surface was immersed for one hour in aerated 10^{-2} M $\text{Na}_2\text{SO}_4 + 10^{-2}$ M PDTC.

The molecular structure of 1-pyrrolidine dithiocarbamate (PDTC) is depicted in Fig. 2. It is interesting to mention that PDTC is a non-toxic and non-hazardous compound [39].

2.2 Solutions and electrochemical tests

The working electrolyte was prepared from analytical-grade reagents (Fluka analytical, 99%): anhydrous sodium sulfate (Na_2SO_4) using distilled water. The experiments were performed in 10^{-2} M Na_2SO_4 solution. PDTC, boric acid (H_3BO_3) and sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7$) were supplied by Sigma-Aldrich. The product purities were 97%, 99.8% and 99.5%, respectively.

The pH employed was 3, 6.1, and 11. Solutions with a pH value of 3 were made using 10^{-2} M Na_2SO_4 acidified with H_2SO_4 , while solutions with pH values of 11 were made using 10^{-2} M Na_2SO_4 adjusted with NaOH.

Atmospheric oxygen served as the source of dissolved oxygen used in the electrochemical tests. In some cases, solutions were deoxygenated by purging for 30 min with nitrogen N_2 (purity 99.999%) or supersaturated by bubbling oxygen O_2 (99.999%) for 30 min. Both N_2 and O_2 gas were purchased from Air Liquide. Oxygen concentration was measured with Eutech's CyberScan 650 multi-parameter equipped with a Clark electrode. In air-saturated and O_2 -supersaturated media, the values of O_2 concentrations were 2.25×10^{-7} and 10^{-6} mol cm^{-3} , respectively.

Fig. 2 Structure of 1-pyrrolidine dithiocarbamate (PDTC)

In deaerated medium, O_2 concentration yielded a negligible value. During electrochemical runs, both purging and bubbling were continuously kept in the cell above the electrolyte.

2.3 Electrochemical measurements

All the measurements were taken at room temperature (298 ± 2 K) in a classic glass cell. The counter electrode was a Pt grid, whereas the reference electrode was a saturated calomel electrode (SCE).

The electrochemical experiments were carried out using a Voltalab PGZ 301 potentiostat/galvanostat. The polarization plots were drawn by linear sweep voltammetry (1 mV s^{-1}) with a rotation rate of the electrode going from 500 to 2500 rpm. The EIS spectra were recorded with an applied frequency domain ranging from 100 kHz to 10 MHz with 10 points per decade. The fitting and analysis of the results were performed by using EC-Lab.

2.4 Surface analyses

2.4.1 X-ray diffraction (XRD)

In order to identify the crystalline phase of the developed films on copper surface after pre-treatments, X-ray diffraction patterns were collected using X-ray diffraction (Siemens D5000) with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) powered at 40 kV and 40 mA. The scanning range is within $2\theta = 10^\circ$ and $2\theta = 80^\circ$ with 0.04 step recorded each 5 s.

2.4.2 Scanning electron microscopy (SEM)/energy-dispersive spectroscopy (EDX)

SEM micrographs were picked up after the different pre-treatments using FEI Quanta FEG 450 scanning electronic microscope (SEM). We have used energy-dispersive X-ray analyzer (EDX, Bruker) with accelerating voltage of 20 kV in order to investigate the elements composing the species accumulated on copper surface.

3 Results and discussion

3.1 Evaluation and characterization of copper surface after pre-treatment

As the surface condition of copper plays a major role in the kinetics of ORR, it is necessary to initially assess and characterize the different surface conditions, namely pre-reduced, passivated and covered with PDTC molecule.

3.1.1 SEM observation and EDX analysis Surface

Figure 3 shows SEM micrographs of copper surfaces after the different pre-treatments (pre-reduced, passivated and covered with PDTC), and Fig. 4 indicates the corresponding EDX analyses. In 10^{-2} M Na_2SO_4 solution, the pre-reduced surface (Fig. 3a) is uniform and is characterized by the presence of scratches caused while pre-polishing the electrode. EDX analysis of the surface shown in Fig. 4a indicates that copper atom is the main element occupying the surface, accompanied by a small fraction of oxygen which indicates the presence of a native oxide layer.

The passivated surface is covered with a copper oxide layer (Fig. 3b). Indeed, Fig. 4b indicates that Cu and O atoms are the main elements of EDX analysis which confirms that the developed layer is principally composed of copper oxides.

In the presence of 10^{-2} M PDTC in solution, it is noticed the presence of a few crystals on the surface (Fig. 3c). EDX spectrum shows the presence of sulfur atom, which implies the adsorption of PDTC molecule and the formation of a layer on copper surface. It is interesting to mention that no trace of oxide was detected after just one hour of immersion in the solution containing 10^{-2} M PDTC

(Fig. 4c). Thus, it can be suggested that the adsorption of the film is rapid enough to prevent the formation of copper oxides.

3.1.2 XRD analysis

X-ray diffractograms recorded for the different copper surfaces are shown in Fig. 5. For a pre-reduced copper surface, the XRD pattern reveals the presence of high-intensity Cu peaks. This result is in agreement with EDX analysis (Fig. 4a) indicating a small fraction of oxygen, which leads us to suggest that the amount of copper oxide is too low to be detected.

On a passivated copper surface, the XRD spectrum shows that the crystalline phase of the surface consists mainly of metallic copper and cuprite Cu_2O observed at angle values of 30° , 36.5° and 61° . This confirms the EDX analysis where Cu and O atoms were the main elements detected (Fig. 4b). These results are in good agreement with those of Qafsaoui et al. [38] who reported that copper oxides were present on an oxidized copper electrode in a borate buffer solution using coulometric measurements. Similarly, Babic et al. [40] stated that passivation of copper in a borate buffer solution was consistent with the formation of a $\text{Cu}_2\text{O}/\text{CuO}-\text{Cu}(\text{OH})_2$

Fig. 3 SEM micrographs of pre-reduced copper surface (a) passivated (b) and covered with PDTC (c)

Fig. 4 EDX analyses of pre-reduced copper surface (a) passivated (b) and covered with PDTC (c)

Fig. 5 XRD patterns recorded on pre-reduced, passivated and covered with PDTC copper surfaces

duplex oxide film. The inner barrier layer being Cu_2O and the aqueous outer layer being a CuO-Cu(OH)_2 complex. In our case, the qualitative analysis did not reveal the presence of the cupric oxide CuO , which is probably related to the fact that CuO amount is low to be detected.

On a surface covered with PDTC, Cu_2O peaks disappear suggesting the absence of oxides. This may be due to the rapid adsorption of PDTC molecules on the surface which prevents the formation of copper corrosion products. The film formed in the presence of PDTC is probably amorphous and cannot be detected using XRD. In a previous work. [39], similar results were found in a study of the inhibition effect of 10 mM PDTC on copper in 0.2 or 30 g L^{-1} NaCl solution.

3.2 Influence of copper surface condition on oxygen reduction reaction kinetics

Here, we present the experiments conducted on copper in 10^{-2} M Na_2SO_4 for the different surface conditions namely pre-reduced, passivated and covered with PDTC.

3.2.1 Pre-reduced surface

3.2.1.1 Polarization curves Representative potentiodynamic curves for ORR on a pre-reduced copper surface obtained in aerated 10^{-2} M Na_2SO_4 medium, as well as the base voltammogram recorded in deaerated solution at 1000 rpm, are shown in Fig. 6a. The curves recording was started from the corrosion potential E_{corr} toward more negative overpotentials at a scanning rate of 1 mV s^{-1} . In deaerated medium, the curve is featureless and the only cathodic reaction taking place is water reduction at -1.4 V/SCE . In aerated medium, the cathodic current presents a well-defined current plateau going from -0.85 V to -1.4 V/SCE and referring to O_2 reduction limitation by mass transport, which is typically representative of ORR on bare electrode surfaces. The polarization curve exhibits a limited current density of about -0.79 mA cm^{-2} at -1 V/SCE and 1000 rpm. It is known that the increase in rotation rates (from 500 to 2500 rpm) shortens the diffusion layer, which clearly induces a progressive enhancement of limiting current densities.

In the overall potential range reported in Fig. 6a, ORR process displays four distinct behaviors. In region (I), oxygen reduction is considered to be under pure charge transfer/kinetic control, region (II) represents mixed mass and charge transfer control, (III) designates mass transfer control and finally region (IV) is attributed to hydrogen evolution.

The rotation speed dependence of plateau current densities suggests that these are combined kinetic diffusion process, and as a result, it is predictable to use the Koutecky–Levich equation [18, 21]:

$$\frac{1}{i} = \frac{1}{i_d} + \frac{1}{i_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{nkFC_{\text{ox}}} \quad (4)$$

B is a constant given by:

$$B = 0.62nFC_{\text{ox}}D_{\text{ox}}^{2/3}\nu^{-1/6} \quad (5)$$

In accordance with Eq. (4), the measured current density i involves two parameters: the current density limited by diffusion i_d and the kinetic current density i_k . Besides, the number of electrons exchanged n , the kinetic current i_k and the heterogeneous reaction rate constant k were determined on the basis of the linear relation between i^{-1} vs $\omega^{-1/2}$, where F is the faraday constant, C_{ox} represents the concentration of oxygen in the bulk (mol cm^{-3}), D_{ox} designs the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) and ν denotes for the kinematic viscosity ($\text{cm}^2 \text{ s}^{-1}$). Over the whole range of negative overpotential belonging to mixed control region and diffusion control region, the graphics of i^{-1} versus $\omega^{-1/2}$ present straight and parallel lines (Fig. 6b),

Fig. 6 Polarization curves (scan rate: 1 mV s^{-1}) for the ORR on pre-reduced copper surface in aerated 10^{-2} M Na_2SO_4 . Scanning direction $E_{\text{corr}} \rightarrow -1.7 \text{ V/SCE}$. **a:** Influence of electrode rotation rate. The dashed curve is recorded in a deaerated medium **b:** Plots of i^{-1} vs $\omega^{-1/2}$ (Koutecky–Levich plot) at various disk potentials. **c:** Variation of kinetic current i_k as a function of potential

which evidences that ORR is first order reaction regarding oxygen on pre-reduced copper surface. The nonzero intercept indicates that ORR is a combined kinetic diffusion mechanism.

All disk current density values utilized in the ensuing Koutecky–Levich representations are derived from the polarization plots illustrated in Fig. 6a. The number of electrons transferred in oxygen reduction process is assessed by the straight lines slopes ($1/B$) as suggested by Eq. (5). Using the values obtained for O_2 solubility in aerated medium ($C_1 = 2.25 \times 10^{-7} \text{ mol cm}^{-3}$ [41]), kinematic viscosity ($\nu = 1.009 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ [21, 33]) and oxygen diffusivity ($D = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [33]), the experimental values of n and i_k are determined; hence, the values obtained from Koutecky–Levich plots are summarized in Table 1. Correspondingly, the number of electrons consumed is found to be predominantly four. Similarly, earlier studies [32–34] stated that O_2 reduction on copper in solutions containing bisulfate anions took place by a four-electron process. This can result either from direct reduction without the formation of intermediates or from a sequence of mechanisms with rapid removal of the adsorbed hydrogen peroxide.

The number of electrons exchanged is increasing as the potential becomes more negative; in this case, the surface is considered to become further free of oxide and adsorbed species which facilitates the process of co-adsorption along with the O–O bond breakage, as claimed by Lu et al. [31] and Jiang et al. [32, 34]. The authors indicated that ORR is mainly controlled by the number of available free copper sites where O_2 molecules can be adsorbed, and showed that the adsorption of large amount of sulfate anions on copper inhibited ORR rate by blocking the active sites for oxygen molecules co-adsorption [32, 34].

Moreover, the Koutecky–Levich plot at -1 V/SCE shows that the kinetic contribution to the total current exhibits a value of $-4.52 \times 10^{-3} \text{ A cm}^{-2}$ and a kinetic constant of 0.058 cm s^{-1} . Tran et al. [37] who investigated ORR on pre-reduced Au in $0.1 \text{ M K}_2\text{SO}_4$ found a kinetic current value of $-3.4 \times 10^{-3} \text{ A cm}^{-2}$ at -1 V/SCE . Jiang and Brisard [34] studies of ORR on copper

yielded a value of $-3.569 \times 10^{-2} \text{ A cm}^{-2}$ at -0.37 V/SCE in O_2 -supersaturated $0.5 \text{ M H}_2\text{SO}_4$.

From Table 1, it is noticeable that with increasing overpotential, the kinetic currents and the kinetic constants increase significantly. Figure 6c displays the evolution of the absolute value of i_k (graphed in a semilog plot) versus the potential belonging to mixed and diffusion control regions. At potential region where ORR is controlled by diffusion, the plot indicates that the kinetic current is no longer an exponential function of the potential as Eq. (6) implies, where $C_{ox}(\infty)$ is oxygen concentration in the bulk, b_c is the Tafel coefficient and V is electrode potential.

$$i_k = -kC_{ox}(\infty) \exp(-b_c V) \quad (6)$$

This observation is in concordance with the results of Tran et al. [37] on bare gold electrode in K_2SO_4 and Jiang and Brisard [34] investigations on Cu(111) in oxygenated H_2SO_4 . The authors found that the evolution of the kinetic current was linear in the kinetic control region, while i_k exhibited constant values in the diffusion control region. It can be concluded that for a faradic reaction controlled by diffusion, the total current is expressed through the Koutecky–Levich equation exhibiting the same values for i_d ; thus, the evolution of i_k cannot follow Eq. (6), and then, the kinetic current does yield almost constant values. This experimental representation of the results highlighted that ORR is in fact a complex mechanism that must be studied according to the potential of the electrode.

3.2.1.2 EIS measurements in the cathodic potential range Further details on ORR may be provided by means of EIS experiments, which were conducted on the pre-reduced copper surface in aerated $10^{-2} \text{ M Na}_2\text{SO}_4$ solution. A selection of Nyquist plots recorded at various potentials in the cathodic range are shown in Fig. 7a at 1000 rpm. In all cases, a single capacitive loop is observed, although two time constants are expected, indicating poorly separated time constants. The first one is attributed to charge transfer resistance, and the other one corresponds to the diffusion of electroactive species. From Fig. 7a, we notice clearly that the responses vary as a function of potential.

The equivalent circuit depicted in Fig. 8 was employed to fit and analyze EIS results. For a pre-reduced surface, the circuit consists of a constant phase element (CPE) describing the presence of the adsorbed layer of sulfate and native copper oxide formed likely in the solution. The CPE is associated with R_f which designates the resistance of the layer of sulfate ions adsorbed on copper cathodic sites. The second CPE accounts for the frequency dispersion of the double layer [42–44] whose impedance is expressed by Eq. (7) [45, 46]:

Table 1 Kinetic parameters of ORR on pre-reduced copper surface in aerated $10^{-2} \text{ M Na}_2\text{SO}_4$

Surface condition	Potential (V/SCE)	n	$i_k \text{ (mA cm}^{-2}\text{)}$	$k \text{ (cm s}^{-1}\text{)}$
Pre-reduced surface	-1.00	3.54	-4.52	0.058
	-1.10	3.60	-4.45	0.057
	-1.15	3.65	-4.60	0.058
	-1.20	3.77	-5.37	0.065
	-1.25	3.78	-5.33	0.065
	-1.30	3.95	-6.84	0.080

Fig. 7 Impedance diagram of pre-reduced copper electrode in aerated 10^{-2} M Na_2SO_4 solution in the cathodic potential range at 1000 rpm. **a** Nyquist representation. **b**: Bode representation $\log(|Z|)$ vs $\log(F)$. **c**: Bode representation ϕ vs $\log(F)$

Fig. 8 Electrical equivalent circuit used for fitting the impedance diagrams for a pre-reduced copper surface in aerated 10^{-2} M Na_2SO_4 solution

$$Z_{CPE} = \frac{1}{Q(j\omega)^\alpha} \quad (7)$$

where $\omega = 2\pi f$, Q has units of $F/s^{\alpha-1}cm^2$ and α is the constant phase element exponent. Regarding the fact that a CPE is described as a parallel combination of a resistor and a pure capacitor, Q may be replaced by the values of capacitance calculated using Brug's formula described by Eqs. (8–9) [47–49]:

$$C_{dl} = (Q_{dl}R_{ct}^{1-\alpha_{dl}})^{\frac{1}{\alpha_{dl}}} \quad (8)$$

$$C_f = (Q_fR_f^{1-\alpha_f})^{\frac{1}{\alpha_f}} \quad (9)$$

The CPE is in parallel with R_{O_2-ads} representing the electron transfer resistance of further reduction in adsorbed ORR intermediate species $(HO_x)_{ads}$ such as H_2O_2 , $OH^\cdot$, HO_2 [32], R_{ct} denotes for the charge transfer resistance of O_2 reduction process from oxygen molecules, Z_{diff} refers to the diffusion impedance represented by the following equation:

$$Z_{diff} = R_d \frac{th(\sqrt{\tau_d j \omega})}{\sqrt{\tau_d j \omega}} \quad (10)$$

where R_d stands for the diffusion resistance ($\Omega \text{ cm}^2$) and τ_d is the diffusion time constant. To discuss and analyze the fitted parameters, the values of R_d were considered.

The values of α_{dl} ranged from 0.81 to 0.85 and the double-layer capacitances from 58 to 79 $\mu\text{F cm}^{-2}$. From impedance spectra recorded at 1000 rpm, the dependence of R_{ct} and R_d on potential is recapped in Table 2. The results illustrate that when the potential shifts to a negative direction, R_{ct} values decrease, while those of R_d increase. This behavior is typical of a Faradaic reaction limited by diffusion of reactive species as indicated by Tran et al. [37] studies of ORR on pre-reduced gold at 900 rpm. They found that ORR occurs through a four-electron pathway for large overpotential at 900 rpm, while forming hydrogen peroxide as an intermediate through an indirect two electron transfer mechanism. However, H_2O_2 formed was rapidly removed from gold surface by convection. Likewise, Lu et al. [32] studies of O_2 reduction in aerated stagnant 0.5 M H_2SO_4 on pre-reduced copper revealed the presence of a first region going from -0.5 V and -0.4 V/SCE where $R_d > R_{ct}$ which revealed that oxygen diffusion controlled the direct ORR process. The authors also observed that in the potential domain ranging from -0.40 V and -0.20 V (region II), the cathodic current density decreased and the diffusion characteristic perceived at low frequencies weakened as the potential became less negative. This was accompanied with an augmentation in R_{ct} and R_{O_2-ads} and a diminution

in R_d values. Lu et al. [32] concluded then that in region II, the diffusion rate increased locally at copper surface, combined with the appearance of a mixed control region, inducing an increase in the indirect process through two electron transfer relatively to the direct pathway because of the adsorption of sulfate anions.

From the electrochemical experiments, we can assume that in the charge transfer control, where sulfate adsorption is prominent, ORR direct reduction by a four-electron pathway is inhibited, while the two electron transfer process is favored. The decrease in current density in the region under mixed/kinetic and kinetic control may be induced by competition for free cathode sites between oxygen molecules and sulfate anions. At more cathodic overvoltages, the active sites are free of adsorbed species as suggested by several studies [23, 32, 34]. In the diffusion control region, we suggest that ORR occurs mainly through a direct process with the formation of small quantity of H_2O_2 , since the number of O_2 adsorption available sites increases at large overpotential. The presence of a single O_2 reduction plateau indicates that diffusion of H_2O_2 and/or its reduction to OH^- is very fast.

3.2.2 Passivated surface

3.2.2.1 Polarization curves In a similar way to the curves drawn on the pre-reduced copper surface, four distinct behaviors are observed in the overall potential range reported in Fig. 9a, though for a passivated surface, the ORR current seems to overlap with the current of hydrogen evolution as the rotation rate increases. Additionally, if compared to the polarization curve for pre-reduced copper surface, a significant difference is noticed in the potential domain where kinetic and mixed control is yielded. Note that higher activity toward ORR induces higher onset potential and a narrower mixed control region. It is also worth mentioning that diffusion limited current is proportional to the oxygen concentration, while the kinetic current is proportional to active sites availabil-

Table 2 Parameters obtained from the fitting of the experimental EIS data for pre-reduced copper electrode as a function of the cathodic potential

$-E/\text{V/SCE}$	$R_e \Omega \text{ cm}^2$	α_f	$C_f \mu\text{F cm}^{-2}$	$R_f \Omega \text{ cm}^2$	$R_{O_2-ads} \Omega \text{ cm}^2$	α_{dl}	$C_{dl} \mu\text{F cm}^{-2}$	$R_{ct} \Omega \text{ cm}^2$	$R_d \Omega \text{ cm}^2$
0.500	61.89 ± 0.29	0.85	8.32 ± 0.05	9.20 ± 0.12	22.09 ± 0.03	0.81	58.25 ± 0.07	645 ± 0.23	78 ± 0.09
0.550	62.96 ± 0.13	0.85	8.79 ± 0.02	10.03 ± 0.06	21.15 ± 0.08	0.81	60.09 ± 0.15	413 ± 0.12	101 ± 0.18
0.600	60.38 ± 1.05	0.88	9.17 ± 0.02	9.59 ± 0.07	19.03 ± 0.16	0.82	59.37 ± 0.26	347 ± 0.03	154 ± 0.05
0.650	61.97 ± 0.15	0.89	9.53 ± 0.01	9.21 ± 0.14	16.32 ± 0.07	0.82	59.42 ± 0.02	209 ± 0.08	221 ± 0.39
0.725	63.21 ± 0.17	0.90	9.64 ± 0.19	8.73 ± 0.18	17.41 ± 0.10	0.83	61.54 ± 0.05	170 ± 0.11	431 ± 0.12
0.800	60.23 ± 0.05	0.91	10.15 ± 0.08	8.62 ± 0.09	16.13 ± 0.25	0.81	65.15 ± 0.07	88 ± 0.04	539 ± 0.41
0.875	60.56 ± 0.24	0.92	10.89 ± 0.21	7.14 ± 0.05	15.09 ± 0.02	0.84	73.28 ± 0.15	80 ± 0.02	1037 ± 0.27
0.925	61.02 ± 0.15	0.92	12.17 ± 0.03	6.03 ± 0.23	14.52 ± 0.04	0.85	79.02 ± 0.05	54 ± 0.26	1533 ± 0.53

Fig. 9 Polarization curves (scan rate: 1 mV s^{-1}) for the ORR on the passivated copper surface in aerated $10^{-2} \text{ M Na}_2\text{SO}_4$. **a:** Influence of electrode rotation rate. The dashed curve is recorded in a deaerated. **b:** Plots of i^{-1} vs $\omega^{-1/2}$ (Koutecky–Levich plot) at various disk potentials. Scanning direction $E_{\text{corr}} \rightarrow -1.7 \text{ V/SCE}$. **c:** Variation of kinetic current i_k as a function of potential

Table 3 Kinetic parameters of ORR on passivated copper surface in aerated $10^{-2} \text{ M Na}_2\text{SO}_4$

Surface condition	Potential (V/SCE)	n	i_k (mA cm^{-2})	k (cm s^{-1})
Passivated surface	−0.75	3.21	−1.79	0.026
	−0.80	3.44	−2.24	0.030
	−0.85	3.65	−2.42	0.031
	−0.90	3.87	−2.56	0.031
	−0.95	3.96	−2.57	0.030
	−1.00	3.99	−2.73	0.031

ity. While taking out the diffusion limitation by increasing the rotation rate, the polarization curves did not yield a perfectly defined plateau, which can lead to think that kinetic transfer is the rate limiting step. Thus, we conclude that copper surface becomes less active toward ORR in the sodium sulfate medium as its surface is more oxidized.

The limiting current yields a value of -0.95 mA cm^{-2} at -1 V/SCE and 1000 rpm , which is slightly superior to the one displayed for a pre-reduced surface. This can result from the fact that the total current is assigned by oxygen reduction on pre-reduced surfaces added to the copper oxide layer reduction rates. As mentioned earlier, in the potential domain ranging from -0.3 V to -0.7 V/SCE , the slow oxygen diffusion is probably caused by the competition for free adsorption sites between O_2 molecules, oxygenated species and sulfate anions [23, 32]. In fact, at more negative overpotentials (beyond -0.7 V), copper surface is considered to be free of adsorbed sulfate anions due to their desorption [23, 32], and as a result, this would facilitate the diffusion and adsorption of O_2 on copper substrate.

Likewise, for a passivated copper surface, the i^{-1} vs $\omega^{-1/2}$ graphs (Fig. 9b) indicated a $4 e^-$ transfer mechanism, exhibiting a kinetic current value of $-2.73 \times 10^{-3} \text{ A cm}^{-2}$ at -1 V/SCE and a kinetic constant of 0.031 cm s^{-1} . Similarly, Vazquez et al. [27] found that at film layering compromising Cu_2O , a four-electron transfer pathway was indicated by the presence of a unique linear voltammetric polarization, which implied that the formation of ORR intermediates was not significant [27]. As illustrated in Table 3, in comparison with the kinetic parameters obtained for a pre-reduced surface (Table 1), we can favor the possibility that copper turn out to be less active toward ORR when its surface is covered with copper oxides.

Vazquez et al. [27] findings are in accordance with the findings presented herein indicating that the presence of a duplex copper layer had an inhibitive effect on the electrochemical reduction on copper. In fact, under specific conditions where cuprous oxide turn out to be stable, the authors suggested a CE mechanism where oxygen

reduction proceeded following sequential steps including Cu_2O oxidation [27]:

There again, the cuprous oxide was electrochemically reproduced by reducing the cupric oxide CuO .

Nevertheless, some of the earliest studies approve the increased catalytic activity due to the reduction of O_2 at different rates where two forms of copper sites are present on the surface. In this case, copper possesses two oxidation states, which makes electron relay possible among neighboring sites having distinctive valence, and led to facilitate electron transfer to O_2 adsorbed on one of the existing sites [24]. However, on a passivated surface, it is suggested that ORR occurs through a parallel process identical to that of Vazquez et al. [27] involving the formation of H_2O_2 followed by its fast reduction, where the surface redox mediator for both O_2 and H_2O_2 reduction was Cu(I) . The mechanism is further complicated due to the adsorption of sulfate anions, lowering available active sites number regardless of the increase in cathodic overpotential.

3.2.2.2 EIS measurements EIS experiments were performed on passivated copper surface in 10^{-2} M Na_2SO_4 to give further information into ORR mechanism in the presence of copper oxide layer. Figure 10a shows Nyquist representations of the results obtained at 1000 rpm in the cathodic potential range. The plots indicate the presence of a depressed semicircle, which may compromise three badly separated time constants, mainly associated with the oxide film, charge transfer process and diffusion of electroactive species.

However, in the mixed control region, the charge transfer loops and those of diffusion are separated, which can be explained by their significant contribution to oxygen reduction process.

The electrical equivalent circuit employed to fit more accurately the EIS results is displayed in Fig. 11. The physical nature of the elements includes a constant phase element attributed to the oxide layer and film resistance R_f denoting for the ionic and electronic leakage through the oxide layer. The parameters C_{dl} and R_{ct} take account of the capacitance of the double layer and the charge transfer resistance. The Z_{diff} component is associated with the diffusion impedance of dissolved oxygen.

C_{dl} and C_f were calculated using Eqs. (8) and (9), respectively. The values of α_{dl} ranged from 0.82 to 0.87, and the

capacitances of the double layer vary on the order of $22\text{--}39 \mu\text{F cm}^{-2}$. The results of the fitted parameters R_{ct} and R_d are presented in Table 4, and exhibit similar behavior to the one observed on the pre-reduced copper surface, although R_{ct} and R_d exhibit higher values than in the case of pre-reduced copper surface. Therefore, we suggest that ORR process is less active on a passivated surface which explains the inhibition of ORR rate observed in the potentiodynamic curves presented in Fig. 9a. In the charge transfer region, $R_{ct} > R_d$ which indicates an increase in diffusion rate coupled with the adsorption of sulfate anions. As we approach the diffusion control regime, R_d increases, while R_{ct} and R_f decrease, which refers to the weakening of charge control ORR kinetics and diminution of the oxide thickness with potential.

From these results, it may be concluded that the main ORR process involves a four-electron process in mass transfer control region, while the indirect process appears to dominate on a passivated surface as it is reported by the values of R_{ct} and R_d in the kinetic control region.

3.2.3 Surface covered with PDTC

3.2.3.1 Polarization curves In the case of copper surface covered with PDTC (Fig. 12a), a clear modification of the polarization curves for ORR under aerated conditions is noticed. The RDE measurements show no significant effect of diffusion on the cathodic current densities.

In the case of copper covered with PDTC, it is interesting to note that the overall current density decreases considerably in absolute value by a factor of 5 (0.17 mA cm^{-2} at -1 V/ECS for a rotation rate of 1000 rpm) if compared to both pre-reduced and passivated copper surfaces. This decrease in current density is accompanied by a shift in potential toward a more cathodic value, from which indicates that O_2 reduction reaction on this type of substrate becomes very difficult.

It is also interesting to point out an important aspect of PDTC inhibition of O_2 reduction on copper electrodes. In fact, PDTC behaves in an irreversible way since once it reacts with the surface, the inhibition remains despite removal of the activity of the inhibiting species by placing the copper electrodes back in the inhibitor free 10^{-2} M Na_2SO_4 solution. Furthermore, according to the plot of the absolute value of the cathodic current density as a function of the potential represented by Fig. 12b, it is striking to notice that PDTC blocks copper active sites and inhibits ORR even when O_2 concentration increases in the medium.

In this case, the rate limiting step of the overall reaction is the low electron transfer rate, which explains the reason why the mass transport control is difficult to reach. In fact, Qafsaoui et al. [55, 56] stated that PDTC acted as mixed inhibitor decreasing ORR rate. Hence, the charge transfer

Fig. 10 **a:** Nyquist representation of impedance diagrams of passivated copper electrode in aerated 10^{-2} M Na_2SO_4 solution in the cathodic potential range at 1000 rpm. **b:** Enlarged spectra recorded

at -500 mV, -550 mV and -600 mV/ECS. **c:** Bode representation of $\log |Z|=f(\log F)$. **d:** Bode representation of $\phi=f(\log F)$

Fig. 11 Electrical equivalent circuit used for fitting the impedance diagrams of passivated copper in aerated 10^{-2} M Na_2SO_4 solution

rate is difficult because of the presence of PDTC barrier film which covers most of the copper sites where oxygen molecules are expected to adsorb.

3.2.3.2 EIS measurements EIS measurements taken on copper surface covered with PDTC in the cathodic potential range at 1000 rpm are depicted in Fig. 13a. The spectra present a flattened semicircle with an increased loop diameter, compared to pre-reduced and passivated surface conditions. This increase in loop diameter reflects the formation of an adsorbed protective film. Although it is difficult to note the presence of a capacitive loop in the high-frequency domain on the Nyquist diagram (Fig. 13a), the Bode diagram (Fig. 13b and c) clearly shows the presence of a capacitive loop at high frequencies above several kHz. In this case, two time constants are considered and are attributed to the presence of the adsorbed film and the double layer and electron transfer process.

Table 4 Parameters obtained from the fitting of the experimental EIS data of passivated copper surface as a function of the cathodic potential

$-E/\text{V/SCE}$	$R_e/\Omega\text{ cm}^2$	α_f	$C_f/\mu\text{F cm}^{-2}$	$R_f/\Omega\text{ cm}^2$	α_{dl}	$C_{dl}/\mu\text{F cm}^{-2}$	$R_{ct}/\Omega\text{ cm}^2$	$R_d/\Omega\text{ cm}^2$
0.45	61.32 ± 0.07	0.72	2.06 ± 0.01	251 ± 0.06	0.82	22.56 ± 0.02	1244 ± 0.09	63 ± 0.10
0.50	61.17 ± 0.05	0.74	2.83 ± 0.04	165 ± 0.03	0.84	24.90 ± 0.02	445 ± 0.14	98 ± 0.02
0.55	61.09 ± 0.14	0.75	3.27 ± 0.04	115 ± 0.05	0.86	21.36 ± 0.05	212 ± 0.01	188 ± 0.04
0.60	61.47 ± 0.29	0.73	3.42 ± 0.27	95 ± 0.26	0.85	33.02 ± 0.06	137 ± 0.07	355 ± 0.06
0.725	61.93 ± 0.02	0.79	3.98 ± 0.12	65 ± 0.22	0.87	36.09 ± 0.11	81 ± 0.03	609 ± 0.04
0.875	61.89 ± 0.03	0.82	4.18 ± 0.08	61 ± 0.17	0.85	32.16 ± 0.08	76 ± 0.03	1055 ± 0.25
0.975	61.73 ± 0.08	0.83	4.96 ± 0.01	54 ± 0.09	0.82	38.79 ± 0.07	61 ± 0.02	2285 ± 0.18

Fig. 12 Polarization curves (scan rate: 1 mV s^{-1}) for the ORR on copper surface covered with PDTC in aerated $10^{-2}\text{ M Na}_2\text{SO}_4$. **a:** Influence of electrode rotation rate. **b:** Influence of oxygen concentration. Scanning direction $E_{\text{corr}} \rightarrow -1.7\text{ V/SCE}$

The EIS spectra were fitted and examined by means of the equivalent circuit presented in Fig. 14. Using Eqs. (8) and (9), C_{dl} and C_f were calculated subsequently. The values of α_{dl} ranged from 0.77 and 0.74, and the capacitances of double-layer values vary from 9 to $14\text{ }\mu\text{F cm}^{-2}$.

The relevant parameters are shown in Table 5. Note that R_{ct} values slightly increase with the decrease in cathodic

overpotential which may indicate that charge transfer becomes more difficult. Similarly, Lu et al. [32] explained the increase in R_{ct} by the lowering of electrochemical drive related at low cathodic potentials, while Kuang et al. suggested that higher R_{ct} values were obtained due to the obstruction of electron transfer process by O_2^- generated from ORR process [36].

In this case, the low charge transfer is considered the ORR rate limiting step of the whole process due to the adsorption of PDTC protective film on copper electrode. In summary, on a surface covered with PDTC, the ORR is strongly inhibited and limited predominantly O_2 deposition at the electrode surface by electron transfer from copper substrate.

3.2.4 Influence of pH on ORR polarization curves

Figure 15 shows the influence of pH on ORR current densities measured at -1 V/SCE as a function of surface condition. For a pre-reduced surface, the current densities are slightly increasing with increasing pH, which may be due to the contribution of bulk oxide Cu_2O reduction to the limited current densities as pH exceeds 6.

On a passivated surface, an increase in cathodic current densities with increasing pH is observed. Previous studies revealed that the increase in pH leads to the formation of a catalytic film, which is supposed to compromise $\text{Cu}(\text{OH})_{\text{ads}}$ and/or submonolayer Cu_2O [20]. Besides, King et al. [24] proposed the possibility that $\text{Cu}(\text{I})$ surface sites were stabilized by adsorbed OH^- . On a surface covered with an oxide film, Ilievare et al. [35] stated that total cathodic current measured for the ORR under mixed control should include the additional rate limitation by electron transfer across copper oxide layer to carry the ORR at the oxide/electrolyte interface. In this case, the total current is expressed by Eq. (14):

$$\frac{1}{i} = \frac{1}{i_d} + \frac{1}{i_k} + \frac{1}{i_{el}} \quad (14)$$

However, for copper oxide layer i_{el} is negligible presumably because the oxide is either highly ionically or

However, for a surface covered with PDTC, no influence of pH on cathodic current densities is detected, which relates to the high stability of PDTC adsorbed barrier layer. In fact, several works highlighted the efficiency of inhibitors containing sulfur atoms in various media with different pH [39, 50–54], as sulfur atom has a strong tendency for copper [55].

Table 5 Parameters obtained from the fitting of the experimental EIS data as a function of the cathodic potential for a surface covered with PDTC

$-E/V/SCE$	$R_e \Omega \text{ cm}^2$	α_f	$C_f \mu\text{F cm}^{-2}$	$R_f \Omega \text{ cm}^2$	α_{dl}	$C_{dl} \mu\text{F cm}^{-2}$	$R_{ct} \Omega \text{ cm}^2$
0.725	66.82 ± 0.13	0.96	0.121 ± 0.04	842 ± 0.29	0.77	9.20 ± 0.03	4958 ± 0.25
0.800	66.81 ± 0.02	0.93	0.123 ± 0.09	831 ± 0.05	0.77	8.97 ± 0.01	3779 ± 0.06
0.875	66.86 ± 0.45	0.94	0.132 ± 0.03	825 ± 0.02	0.75	9.43 ± 0.08	3385 ± 0.21
0.950	66.91 ± 0.06	0.94	0.139 ± 0.16	812 ± 0.02	0.76	10.17 ± 0.11	2298 ± 0.17
1.000	66.85 ± 0.21	0.91	1.142 ± 0.12	782 ± 0.08	0.75	12.84 ± 0.07	1409 ± 0.01
1.075	66.88 ± 0.33	0.92	1.151 ± 0.07	735 ± 0.20	0.74	14.13 ± 0.04	747 ± 0.05

Fig. 15 Oxygen reduction current densities measured in 10^{-2} M Na_2SO_4 as a function of pH and surface condition on copper at 1000 rpm (left scale: pre-reduced and passivated; right scale: covered with PDTC)

4 Conclusions

The influence of copper surface condition on the ORR process in 10^{-2} Na_2SO_4 was examined by electrochemical methods. From the experimental results, several deductions can be made:

- ORR is strongly affected by the properties and especially the state of the surface. The ORR rate increases in the subsequent order: Covered with PDTC < passivated < pre-reduced surface.
- On pre-reduced copper surface, ORR occurs through a four-electron pathway mainly controlled by oxygen diffusion, though sulfate anions plays a major role at more anodic potentials.
- On passivated copper surface, oxygen reduction is less active and is influenced by a combination of ORR rate and copper oxide reduction.
- For both pre-reduced and passivated surface conditions, the electron transfer resistance decreases when the reaction overpotential is more negative, as it is expected for a Faradaic reaction controlled by diffusion.

- The surface covered with PDTC exhibits the least active site for ORR since the current density decreased significantly due to the presence of PDTC adsorbed layer, which is found to yield high stability regardless of pH value and O_2 concentration.

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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