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Surface tension of Cu-O alloys at 1400 K

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Critical to understanding and controlling phase mixing and separation in metallurgical processes, is the development of reliable experimental techniques to measure interfacial properties of melt systems. A series of experiments has been carried out to determine the effect of oxygen potential on the surface tension of liquid copper. Using an electromagnetic levitation method, a surface tension-oxygen chemical potential adsorption isotherm was produced for the Cu-O system at T ~ 1400 K. The surface tension results show good agreement with the literature values e.g. within 3 per cent for pure copper. The Belton 'ideal' adsorption isotherm was applied, and the following equation derived to best fit the experimental data :

$$\gamma = 1251 - 77.5\ \ln\left[1 + \left(2.79x10^5 \cdot pO^{1/2}\right)\right]\left(mN.m^{-1}\right)$$

Using this equation, the surface tension of copper was calculated/predicted as a function of oxygen potential at 1400 K, and showed excellent agreement with the experimental values. This confirmed that the adsorption behaviour of oxygen in liquid copper is ideal. The saturation coverage of oxygen on the surface of liquid copper was determined to be Γ_o = 6.65 μmoles.m,$^{-2}$ corresponding to an area per adsorbed oxygen atom of $\alpha_o \approx 25$ Å^2. These values agree well with those cited in the literature, and our experimental data cover a very wide range of oxygen potential (10^{-5} to 10^{-17} atm).

Keywords: levitation melting, surface tension, Cu-O alloys, oxygen potential, adsorption isotherm, surface coverage.

Introduction

In well-stirred smelting vessels, intimate contact between reacting phases occurs, so a good understanding of phase mixing and separation is needed to ensure high productivity is maintained. This knowledge can be used to minimize copper losses to the slag, remove non-metallic inclusions from the primary metal, or control splashing and foaming, for example. Critical to achieving this understanding and control of phase mixing and separation is the development of reliable experimental techniques to measure interfacial properties of melt systems. It is now well known that strongly adsorbed solutes can sometimes lower the rates of chemical reactions between gases and liquid metals.[1,2] Group VI elements are known to be strongly surface active.[3] Of these, oxygen and sulphur are commonly present at a significant chemical potential in pyrometallurgical refining processes. Therefore, a practical imperative exists to obtain a quantitative understanding of the interplay between strong adsorption and kinetics at the gas-liquid interface, which can influence this rate of refining.

The adsorption of a strongly surface active solute can be considered in terms of the combined form of the ideal (site-fillage) Langmuir isotherm, with the Gibbs adsorption isotherm.[4] The resulting equation for the depression of surface tension (spreading pressure) of a liquid metal by a solute such as oxygen, can be expressed as :

$$\gamma_o - \gamma = RT\Gamma_o\ \ln\left(1 + Ka_o\right) \qquad [1]$$

where for liquid Cu-O, $\gamma_o - \gamma$ represents the depression of surface tension of pure liquid copper, R is the gas constant , T is sample temperature (Kelvin), Γ_o is the saturation surface coverage by oxygen, a_o is the bulk activity of oxygen, and K is the Langmuir adsorption coefficient.

Traditionally, the adsorption behaviour of a solute in a liquid metal has been studied by measurement of the surface tension of the metal as a function of composition. Available information from surface tension studies show oxygen in liquid copper to be very surface active. Measurement of surface tension of metals, such as copper, is no easy task, as any slight contamination of the surface by other species (such as Si or S), can dramatically influence the surface tension. The widely used Sessile drop method can suffer from contamination of the metal sample from contact with the substrate (such as copper resting on alumina), and also the need to obtain an accurate profile of the droplet. However, in this method, temperature measurement is considered to be very accurate due to the use of direct contact thermocouples.

Electromagnetic Levitation Melting (EML) is a containerless processing technique for use on electrically conductive materials such as metals. The main advantage of this technique is the avoidance of contamination or chemical reaction with the sample container walls. Disadvantages of EML are the need for contactless temperature measurement (using optical pyrometry), and the need to design a suitable coil for levitating the droplets in a stable manner. A historical shortcoming of EML has been the determination of the different oscillation modes of the drop using photometric detectors. This has been ameliorated with the recent development of a high-speed digital image processing technique[5] (applied in this work), which can unambiguously identify the relevant oscillation modes.

Objectives of the surface tension study were to:

- Apply the EML method to systematically measure the surface tension of liquid copper, as a function of oxygen potential at T ~ 1400 K
- Create a surface tension adsorption isotherm, in order to establish a detailed dependence of oxygen activity on the surface tension of liquid copper
- Apply the Belton equation in order to determine the 'ideality' of oxygen adsorption in liquid copper at 1400 K.

Although copper smelting processes generally operate between 1470 and 1570 K, an experimental temperature of T ~ 1400 K was chosen for this study, to enable comparisons between our surface tension measurements and those documented in the literature.

Experimental apparatus and procedures

Electromagnetic Levitation Method (EML)

A schematic of the EML apparatus can be seen in Figure 1. A 25 kW, 400 kHz solid-state induction unit was used to levitate and melt the copper samples, having a mass of 0.5–0.8 g. The water cooled levitation coil was constructed of copper tubing (3 mm OD x 2.3 mm ID), sheathed in a glass wool sleeve to prevent short-circuiting, and was wrapped around a silica work tube (15 mm OD x 10 mm ID), fitted with rubber O-ring seals at each end for gas isolation. The metal samples used were either high purity (99.999 per cent), or standard purity copper (99.98 per cent). Samples were loaded into a small silica cup, housed inside a gas-tight rotating sample chamber. A purging gas of 5 per cent H_2 in argon was introduced into the work tube at a flow rate of ~ 5 litres.min.$^{-1}$ Once the induction unit was operating, the sample was vertically positioned inside the levitation coil using an alumina push rod. As soon as the copper sample was observed to begin melting, the gas flow was increased to ~ 7 litres.min^{-1} to keep the sample molten and stable at a temperature of ~ 1400 K. It has been previously stated that the most reliable values of surface tension are often obtained after metal deoxidation treatments of several hours. For instance, high partial pressures of hydrogen,[6] or UHV melting facilities can be used to remove dissolved gases such as oxygen.[7] In the current study, it was not possible to run the EML apparatus for more than about 40 minutes, due to overheating of the copper 'buzz bars' connecting the induction unit to the levitation coil. Using a 5 per cent H_2-Ar gas mixture, a pre-treatment time of about 10 minutes was used to remove residual oxygen from the copper samples, prior to equilibration under reaction gas mixtures (CO_2/CO), usually for an additional 20 minutes. Incidentally, following a prereduction/deoxidation step using hydrogen containing gas, the lower purity copper bar was found to be just as 'clean' as the very high purity copper i.e., the surface tension values obtained were often identical.

Reaction gases such as food grade CO_2 and high purity CO were purified and blended using an in-house gas cleaning and metering apparatus. Mass flow controllers were used to meter the gases, which were initially cleaned by passing through a silica gel and magnesium perchlorate packed column for moisture removal, then through copper turnings heated at 500°C for residual oxygen removal, then finally through a 5Å molecular sieve (BDH, 3 mm pellets of crystalline calcium aluminosilicate). The mass flow meters were precalibrated, while the silica gel, heated copper turnings and magnesium perchlorate were regularly regenerated.

In order to determine the influence of oxygen potential on the surface tension of liquid copper, the fugacity of oxygen was fixed by controlling the ratio of carbon monoxide to carbon dioxide, according to the reaction[8]: $2CO(g) + O_2(g) = 2CO_2(g)$, where $\Delta G^o = -564840 + 173.3T$ (J.mol^{-1}). The flow rate of reaction gases was often high, due to the CO_2/CO ratios required to achieve very low oxygen potentials (eg. $CO_2/CO \sim 0.013$); however, cleaning and

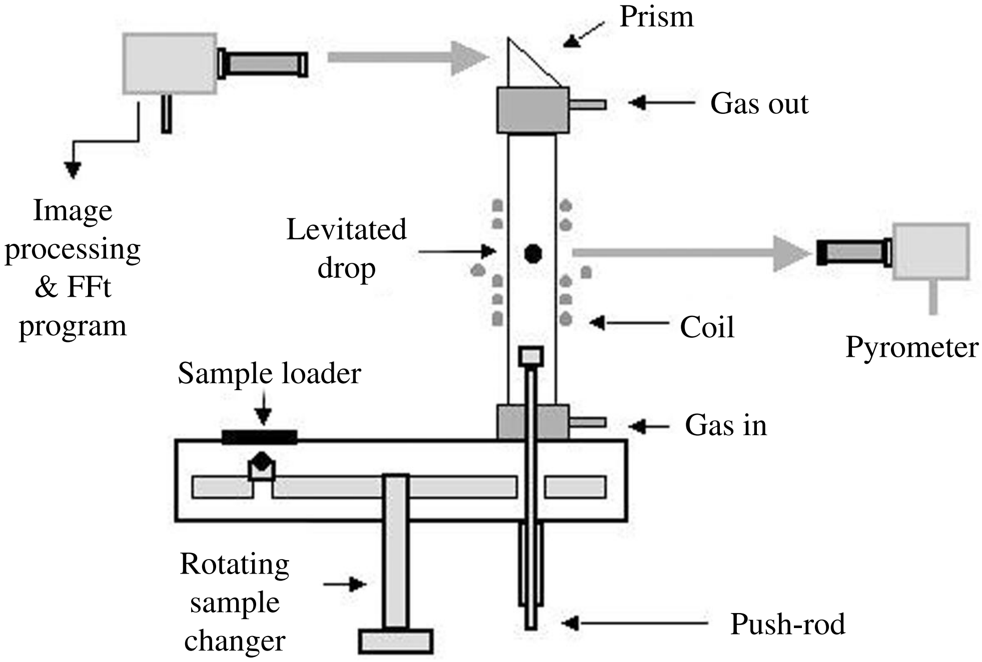

Figure 1. EML and high-speed video imaging facility for measuring oscillation frequency of copper droplets

deoxidation of the gases were effective. For instance, at p_{O_2} ~ 10^{-15} atm, experiments were performed using a total gas flow rate of ~ 2 $l.min^{-1}$ and also ~ 9.5 $l.min^{-1}$ to determine any influence of gas flow rate on the surface tension of molten copper. Here, the large variation of gas flow resulted in little difference in surface tension (~ 1 per cent).

The temperature of molten copper droplets was measured using a disappearing filament optical pyrometer (Chino IR-U), previously calibrated against a heated platinum strip located inside a muffle furnace (equipped with a viewing window). Upon melting, the temperature of the copper sample increased very quickly, so the gas flow rate was increased to maintain the temperature at ~ 1400 K. This was in fact the lowest repeatable temperature that could be recorded for the copper droplets when using the EML apparatus. For instance, at temperatures lower than 1400 K, the samples often started to solidify and become unstable in the field. Therefore, an average value of T ~ 1400 (± 20) K was subsequently used to construct the adsorption isotherm, and in the theoretical calculations. The density of copper, required in the surface tension calculations, was estimated using the following equation[9]: $\rho = 9.37 - T\,(9.442 \times 10^{-4})$, where ρ is the melt density ($g.cm^{-3}$) and T is the melt temperature (Kelvin).

Image processing method and calculation of surface tension

Video images of the molten copper droplets were recorded with a high-speed digital video camera (Redlake Imaging Motion-scope). Using a 90° glass prism positioned at the top of the silica work tube, and close-up lens system, the droplet images were projected onto a 480 x 420 pixel array, and recorded for 16 seconds at 125 frames per second (Figure 1). A Visual Basic digital image processing and Fast Fourier Transform (FFT) program were then used to process the sequential bitmaps (2048) in order to determine the frequency of surface oscillations on the molten droplets. For a detailed description of determining the different oscillation modes of the droplet using image processing, the reader is referred to the work of Sauerland *et al.*[5] The oscillation frequencies, sample mass, and density were then used to calculate the surface tension according to the following equation:[10,11]

$$\gamma = M\frac{3}{32\pi}\left(\frac{1}{5}\sum_{m=-2}^{m=2}\omega_m^{\,2} - \omega_\tau^{\,2}\left(1.9 + 1.2\frac{z_o^{\,2}}{a_r^2}\right)\right) \qquad [2]$$

Here, M is the sample mass, and ω_m represents the frequency of the five surface oscillation modes ($m = 0, \pm 1, \pm 2$) observed in the FFT spectra. The subtracted term on the right hand side, $\omega_\tau^2 = 1/3\,(\omega_{//}^2 + 2\omega_\perp^2)$, is the mean square of frequency of the lateral and axial translational oscillations of the droplet centre of mass (also observed in the FFT spectra); while z_0 is the position of the sample in relation to the zero-point of the magnetic field, and a_r is the radius of the sample. The ω_τ^2 term is subtracted to account for the apparent increase in the translational movement of the drop, due to the action of the applied magnetic field. Until recently, levitated drop measurements did not take into account the action of the applied magnetic field i.e., ω_τ in Equation [2] was neglected, and ω_m simply represented the mean of all of the observed/measured frequencies. In the present experiments, the $m = \pm 1$ modes were found to be degenerate. Therefore, the mean value of ω_m^2 was obtained by taking the average of the $m = 0$ and the $m = \pm 2$ modes only.

Results and discussion

Influence of oxygen potential on surface tension of copper at 1400 K

Figure 2 summarizes the experimental results, where the surface tension of Cu-O alloys is plotted as a function of oxygen potential, from $p_{O_2} = 10^{-5}$ to 10^{-17} atm at T ~ 1400 K. The surface tension steadily increases with decreasing oxygen potential (looking right to left on the x-axis), until reaching a transition/plateau region at p_{O_2} ~ 10^{-12} atm, where the surface tension becomes constant. Figure 3 shows a comparison of our EML results on liquid copper,with those obtained by various authors at similar

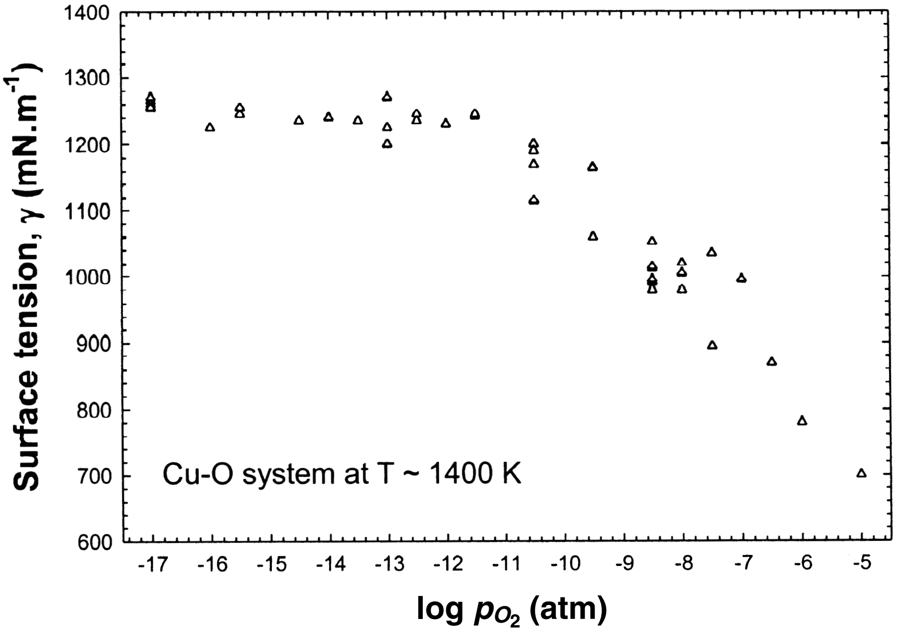

Figure 2. Surface tension-oxygen chemical potential isotherm for the Cu-O system at T ~ 1400 K

temperature and oxygen potential, using the Sessile drop method.[6,12–17] At high oxygen potential our results appear slightly lower than the data of O'Brien and Chaklader[13] and Gallois and Lupis[6] (at 1381 K), while in the region of low oxygen potential, our data appear slightly higher than the values of Morita and Kasama.[14] The literature data involved use of the Sessile drop method, where copper samples were generally deoxidized for several hours prior to introduction of reaction gases. As already mentioned, extensive sample deoxidation was not possible in the current study due to overheating of the levitation apparatus. Overall, the EML surface tension data in Figure 3 show good agreement with the literature, particularly if one considers the very wide range of oxygen potentials employed in the present work.

Our study required use of a non-contact method for measuring sample temperature (optical pyrometry), which is not as reliable as contact thermocouple methods. Control of temperature during EML can be difficult, and often depends on gas flow rate. The average temperature of the present surface tension study was assumed to be T ~ 1400 ± 20 K. Some scatter in our values of surface tension can be observed from Figures 2 and 3, and this is likely to be due to the temperature differences between experiments. For instance, temperatures for the experiments actually varied from 1383–1433 K, which is why an average value of 1400 ± 20 K was chosen for the isotherm. Incidentally, temperatures higher than this would be expected to only slightly decrease the surface tension of copper due to a negative surface tension temperature coefficient. For instance, the coefficient has been reported to vary between $d\gamma/dT \sim -0.2$ to -0.3 $mN.m^{-1}.K^{-1}$ depending on the method used.[17,18]

Application of the Belton ideal adsorption isotherm at 1400 K

Using the standard state of the oxygen activity as $p_{O_2}^{1/2} = 1$ $atm^{1/2}$, the adsorption isotherm in Equation [1] can be slightly modified to:

$$\gamma_o - \gamma = RT\Gamma_o \ \ln\left[1 + K \cdot pO_2^{1/2}\right] \qquad [3]$$

Using this equation, a 3-parameter curve fitting procedure was undertaken in order to determine values for Γ_o and the Langmuir adsorption coefficient, *K* at 1400 K. The best results obtained from the curve-fitting were:

$$\gamma = 1251.1 - 77.4627\ln\left[1 + \left(2.7904x10^5 \cdot pO_2^{1/2}\right)\right] \qquad [4]$$
$$\left(mN.m^{-1}\right)$$

from which γ_o = 1251.1 $mN.m^{-1}$, $\Gamma_o = 6.65 \times 10^{-6}$ mol. $m,^{-2}$ and $K = 2.7904 \times 10^5$ at 1400 K. Note the curve-fitted value for the surface tension of pure copper (γ_o = 1251.1 $mN.m^{-1}$) agrees with the average surface tension of pure copper measured in this study.

Using Equation [4], the surface tension was then calculated as a function of oxygen potential at 1400 K. The results are shown in Figure 4, where the calculated surface tension of copper, obtained by applying the Belton equation, can be directly compared with that measured experimentally, over the very wide range of oxygen potential. There is excellent agreement between the values i.e., the experimental data show the characteristic ideal adsorption behaviour of a surface-active agent in liquid metal.

Saturation coverage of oxygen in liquid copper at 1400 K

The saturation coverage of oxygen on the surface of liquid copper can be defined using the Gibbs adsorption equation:

$$\Gamma_o \approx -(2/RT)\cdot\left(\partial\gamma/\partial \ln pO_2\right) \qquad [5]$$

From the calculated value of ($RT\Gamma_o$) ≈ 77.5, the saturation coverage was determined to be Γ_o = 6.65 $\mu moles.m^{-2}$ at 1400 K, while the area per adsorbed oxygen atom is $\alpha_o \approx 25$ Å^2. Here, $\alpha_o = (\Gamma_o N_A),^{-1}$ where N_A is the Avagadro constant (6.023×10^{23} mol^{-1}). Gallois and Lupis[6] used this equation to derive the saturation coverage from their data, for p_{O_2} between 10^{-12} and 10^{-5} atm at 1381 K. Our values of Γ_o and α_o compare favourably with those of Gallois and Lupis, who obtained Γ_o = 5.72 $\mu moles.m^{-2}$ and $\alpha_o \approx 29$ Å^2 respectively.

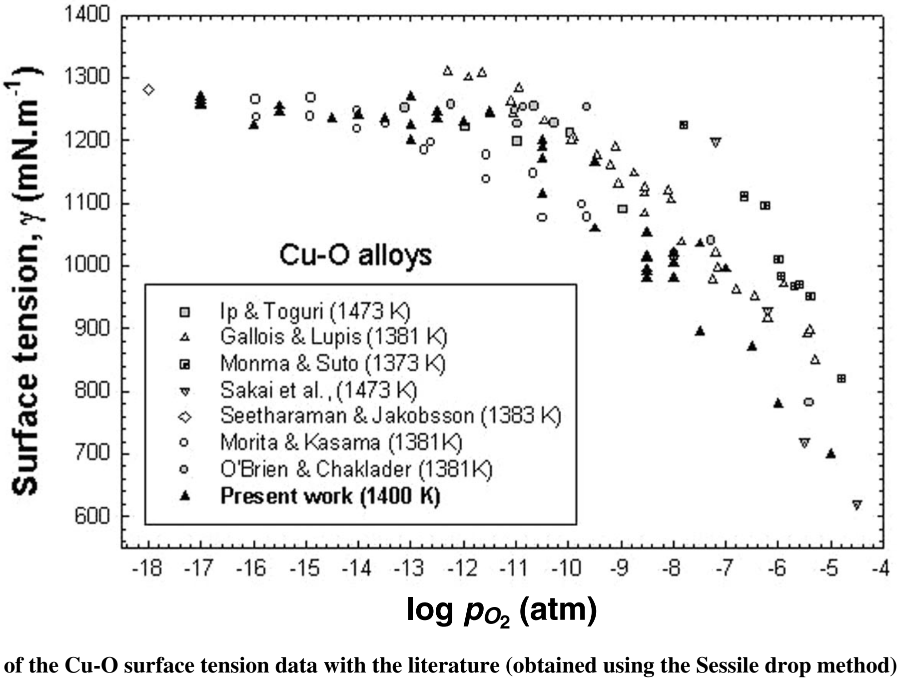

Figure 3. Comparison of the Cu-O surface tension data with the literature (obtained using the Sessile drop method). Note the present EML measurements cover a very wide range of p_{O_2}

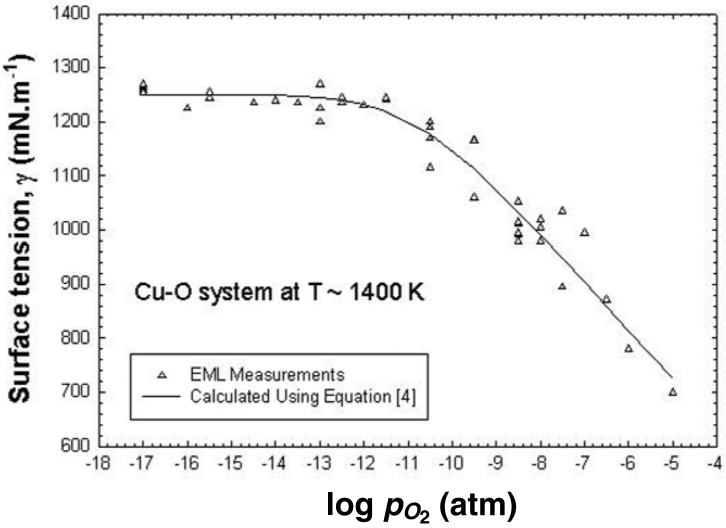

Figure 4. Comparison of Cu-O surface tension data, with that calculated using the Belton ideal adsorption isotherm

Overall, the results demonstrate the successful validation of the EML experimental data against the Belton adsorption isotherm—used to determine the ideality of oxygen adsorption on the surface of liquid copper. It should now be possible to apply this knowledge to predict the dependence of γ against p_{O_2} (or a_o), under more realistic copper-making conditions e.g. higher temperature and sulphur present in the metal phase. Future work involving the technique developed could include a systematic study of the influence of sulphur on the surface tension of copper, under varying oxygen potential, to determine any 'joint' effect (additivity). This information could then be used to determine whether any competitive adsorption behaviour exists between oxygen and sulphur, which may influence the reaction kinetics, and hence rate of copper refining.

Conclusions

A series of experiments to study the influence of oxygen adsorption on the surface tension of liquid copper at 1400 K has resulted in the following outcomes:

- Using an Electromagnetic Levitation Method, a surface tension-oxygen chemical potential adsorption isotherm was produced for the Cu-O system at T ~ 1400 K. The results agreed well with previous literature studies
- The Belton 'ideal' adsorption isotherm was applied, and the following equation was derived to best-fit the experimental data: $\gamma = 1251–77.5 \ln[1 + (2.79 \times 10^5 \bullet p_{O_2}^{1/2})]$ (mN.m^{-1})
- Using this equation, the surface tension of copper was calculated/predicted as a function of oxygen potential at 1400 K, and showed excellent agreement with the experimental surface tension values. This confirmed that the adsorption behaviour of oxygen in liquid copper is 'ideal'
- The saturation coverage of oxygen in liquid copper at 1400 K was calculated to be $\Gamma_o = 6.65$ µmoles.m^{-2}, which corresponds to an area per adsorbed oxygen atom of $\alpha_o \approx 25$ Å^2. These values agree well with those cited in the literature, and our experimental data actually cover a much wider range of oxygen potential.

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