Calculating the coverage of saturated and sub-saturated layers of carbon monoxide adsorbed onto platinum

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Abstract

Adsorption and subsequent stripping of CO_{ads} from catalyst surfaces is an important process used in the determination of active surface area in a range of electrocatalyst systems. Crucial to this process is a measure of how to relate the stripping charge to the actual amount of CO which was adsorbed. In this paper a new experimental approach to measure CO coverage is introduced. By utilising an impinging jet (wall-jet) irrigation system with microelectrodes it is possible to operate under conditions of uniform access. This approach is used to accurately determine the saturated CO_{ads} adlayer coverages using coulometric methods alone even in the presence of background Faradaic processes. A method for determining sub-saturated CO_{ads} adlayer coverages prepared either by partial admission, or partial oxidation of a saturated adlayer is also presented. This approach is used to assess CO_{ads} adlayer coverage on platinum. It is shown that at a CO admission potential of 100mV failing to take into account the charges associated with CO adsorption, and only using the charges measured during the CO_{ads} oxidation would result in an 34% underestimate of the CO_{ads} coverage. A saturated coverage of CO on Pt of 0.68 is found, and these saturated layers are shown to be stable over a period of at least 100 minutes in the presence of low concentrations of oxygen (45 nmol dm⁻³). The CO adsorption transient is experimentally determined at 298K, and a mathematical expression for the CO coverage with time under conditions of defined mass transport is derived. Fitting the experimental data to the theoretical adsorption transient equation yields a value for the CO adsorption rate constant, k_{ad} of 0.0086 cm s⁻¹.

Keywords: CO, carbon monoxide, oxidation, adsorption, platinum, electrode, surface, catalyst, fuel cell

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1 Introduction

Calculation of the absolute CO_{ads} coverage on transition metals, for instance Pt, is difficult [1]. The difficulties have been commented on since 1965 when Brummer and Ford [2] sought to clarify some discrepancies in the charges associated with oxidising complete CO_{ads} adlayers in the work by Gilman [3], and Warner and Schuldiner [4], by correcting for oxide formation and double layer charging.

Weaver et al. [5] reported the maximum coverage for a saturated CO_{ads} adlayer on Pt(111) in perchloric acid to be $\theta_{\text{CO,max}} = 0.6\text{-}0.7$. This was stated to be in contrast to that reported by Feliu et al. [6] for saturated CO_{ads} adlayers on Pt(111) in sulphuric acid with coverages of $\theta_{\text{CO,max}} = 0.9 \pm 0.1$. Although at the same time Feliu et al. also corrected their own results in a paper presenting a novel charge displacement technique [7] which was used in subsequent papers [8, 9]. Weaver et al. [5] conducted an evaluation of the coverages reported in the literature for saturated irreversibly adsorbed CO_{ads} adlayers on low-index Pt using both electrochemical and non-electrochemical methods; such as thin-layer IR spectrophotometry (FTIR), scanning tunnelling microscopy (STM), low-energy electron diffraction (LEED) and studies in ultrahigh vacuum (UHV). This led them to consider the maximum coverage to be no greater than 0.75, and any higher numbers obtained through electrochemical determinations are because not all Faradaic and Non-Faradaic processes have been taken into consideration. Therefore they concluded that in order to estimate reliable coverages it is necessary to provide independent checks using non-coulometric methods, or a more careful widespread consideration of all the factors responsible for the limitations of the existing coulometric methods. Often, the suppression of the hydrogen desorption peaks on Pt is used to determine CO_{ads} coverage, where maximum suppression corresponds to maximum coverage, however this cannot be used to determine absolute saturation coverage and only gives a relative coverage. In addition it does not take into account any double-layer, anion adsorption or other charging effects. In 1998 Weaver and Feliu et al. [10] wrote a paper reviewing the double-layer charge-correction method which is still considered as the authoritative text on this subject to this date. This work presented in this paper builds on that technique and discusses its application to the calculation of sub-saturated layers of carbon monoxide on platinum.

In summary, it is possible to calculate the charge associated exclusively with CO_{ads} oxidation provided all the charges associated with both admitting and oxidising a CO_{ads} adlayer are measured [1, 10, 11]. Despite this, it is still possible to see CO_{ads} coverages calculated using the CO_{ads} oxidation peak alone [12]. In addition, background Faradaic processes often occur which can cause difficulty in accurate calculation. Calculating partial adlayer coverage is often done by comparing the stripping charge to that for a saturated adlayer [13].

As we move from model electrodes (i.e. single crystal) towards real electrocatalysts (nanoparticles), there is a significant change in surface morphology. The number of step and defect sites increases dramatically, and thus there is a much greater heterogeneity in the type of surface site. Although single crystal electrodes are the easiest to characterise, we were concerned with establishing reliable techniques for real electrocatalysts, and in particular for fuel cell catalysts [14] and as such have focussed on polycrystalline electrodes.

In this work we develop an approach to determine accurate CO_{ads} adlayer coverages using coulometric methods alone with the aim of developing accurate approaches for use with highly dispersed electrocatalysts. We apply this approach to the determination of CO_{ads} coverage on platinum. This approach allows the accurate determination of the saturated CO_{ads} adlayer coverage even in the presence of background Faradaic processes. We also show how this approach may be used to produce and determine sub-monolayer coverages of CO_{ads} .

2 Experimental

H_2SO_4 (Merck, Aristar), nitrogen (Air Products, BIP grade), hydrogen (AIR Products, UltraPure grade) and carbon monoxide (BOC, standard grade) were used as obtained. All solutions were 0.5 mol dm^{-3} H_2SO_4 and were prepared with Milli-Q water (18.2 $\text{M}\Omega\text{ cm}$). All the experiments were conducted at a temperature of 25°C ($\pm 1^\circ\text{C}$). All current densities reported are in terms of the electrochemical surface area of the electrode, calculated from the hydrogen adsorption and desorption charge ($Q_{H_{\text{upd,adsorption}}}$, $Q_{H_{\text{upd,desorption}}}$), and the number of surface platinum atoms per unit area (N_0) multiplied by Faraday's constant - a charge density of 210 μCcm^{-2} for a monolayer of adsorbed hydrogen on platinum [15]:

$$\text{Equation 1. } A_{\text{electrochemical}} = \frac{\left(\frac{Q_{H_{\text{upd,desorption}}} - Q_{H_{\text{upd,adsorption}}}}{2} \right)}{N_0 F}$$

2.1 The impinging jet

An impinging jet flow cell configuration relying on one out of several different gravity-fed electrolytes being selected by a motorised switch was used to irrigate the working electrode, Figure 1. This configuration is similar to that previously described [16, 17]. The impinging jet configuration enables electrochemical experiments to be carried out in very clean and reproducible conditions. By nature of the configuration the electrode is irrigated with fresh electrolyte continuously. The electrolyte bathing the electrode may be quickly changed whilst maintaining full electrochemical control of the system. It is thus ideally suited to study electrochemical surface modification and the resultant effects on reactions or processes [17].

2.2 Cleanliness

The cleanliness of the system is extremely important when investigating the oxidation of CO_{ads} on Pt. Some workers have considered that CO is such a strong adsorbate that it will displace any potential contaminants [11], however this has been shown to be not completely true, with a competitive adsorption between CO_{ads} and H_{ads} existing at potentials within the hydrogen region [18-24]. Cleanliness is crucial in observing this phenomenon. Indeed one of the earliest papers to witness the early onset of CO_{ads} oxidation and assign it to the formation of free sites in the CO_{ads} adlayer formed at admission potentials within the hydrogen region, may well have witnessed the early onset due to the extremely high cleanliness levels needed for their single crystal preparation [25].

In this paper the criteria of cleanliness for Pt electrode surfaces as described by Conway et al in 1973 was adopted [26]. The following procedures and precautions were taken to ensure cleanliness. All glassware, reservoirs, pipes, connectors, valves and internal cell components were soaked in-situ in acidified permanganate solution overnight, rinsed with acidified peroxide solution and then rinsed at least 7 times with water prior to use. No contact with any internal components was allowed once the cleaning procedure was started, and any accidental contact required the procedure to be restarted. 6N rated regulators, steel pipes, and PTFE lined steel hoses were used for the gas lines and the cell and reservoirs were always maintained at positive pressure. Electrolyte flow was maintained continuously throughout operation, and all components in contact with electrolyte were fabricated from glass or PTFE.

It was possible to achieve consistent levels of cleanliness characterised by less than 5% loss of the hydrogen desorption charge after potentiodynamic sweeping between 0.05V to 0.40V over a period of 1 hour, and it was possible to maintain the cleanliness of the system at such levels continuously for over 2 weeks.

2.2.1 The importance of suppressing background faradaic processes

As many of the adsorption processes may take 10's of seconds to complete, and the currents associated with those processes due to anion displacement and double layer restructuring are very small, it is important that any background faradaic processes are suppressed. As great care was taken to remove any contaminants, it was found that the main issue was associated with very small levels of adventitious oxygen despite the cell being under a positive pressure of nitrogen and all solutions having been degassed for at least 1 hour prior to investigation.

The amount of oxygen in the system was estimated by comparing the diffusion limiting *ORR* (oxygen reduction reaction) current to the diffusion limiting *hor* (hydrogen oxidation reaction) current in a H_2 -saturated solution for the same electrode under the same conditions and assuming that the oxygen was being reduced under diffusion limiting conditions.

Equation 2.
$$c_{O_2} = -c_{H_2} \times \frac{i_{orr} n_{hor}}{i_{hor} n_{orr}} \times \frac{D_{H_2}}{D_{O_2}}$$

An average diffusion limited *ORR* current from 5 experiments of 1.6 nA (4 μAcm^{-2}) was achievable after completely oxidising a monolayer of CO_{ads} at 700 mV and returning to 100 mV for 120 s using the 125 μm electrode. A diffusion limited *HOR* current of 26.8 μA (70 mAcm^{-2}) was achievable using the same electrode. Utilising literature values for hydrogen concentration and diffusion coefficient of $7.2 \times 10^{-4} \text{ mol dm}^{-3}$ [27] and $3.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [28], respectively and a diffusion coefficient for oxygen of $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [29], an oxygen concentration of $45 \times 10^{-9} \text{ mol dm}^{-3}$ is calculated using Equation 2.

The nitrogen used in the experiments was AIR Products BIP N_2 which is certified to contain less than 10 ppb of O_2 . Therefore it is assumed that some oxygen must be entering the cell from elsewhere. In comparison to the concentration for saturated oxygen of $2.6 \times 10^{-4} \text{ mol dm}^{-3}$ reported [30] the value here is roughly 0.017% of the saturated value. The most likely candidate for O_2 entering the solution lines is through the PTFE parts of the rotary valve, as PTFE has a high O_2 permeability.

Even this very small concentration of oxygen can have a profound effect upon calculating CO_{ads} coverages, and unless it is taken into account can lead to very significant errors as demonstrated below.

2.2.2 Electrode manufacturing

Whilst using bead electrodes of the type described by Bergelin et al. [17] we observed behaviour consistent with the presence of small amounts of CO in the second scan of the cyclic voltammograms after oxidation of CO_{ads} adlayers in the presence of N_2 -saturated solution. This suggested that such electrodes appear to maintain a reservoir of stagnant solution at the boundaries of the meniscus that could harbour contaminants, in particular dissolved CO that had been introduced during the admission phase. The contaminants could then adsorb onto the area of the electrode exposed to the stagnant solution even after electrochemical cleaning. Bead electrodes were therefore replaced with microelectrodes produced by sealing Pt wire into soda glass tubes. In addition this also made it possible to achieve uniform access of reactants to the electrode as described in section 2.2.3.

Production of electrodes used an improved method, broadly based on that described by Wipf et al. [31]. Briefly, custom made high purity soda glass tubes (3.0mm o.d. 1.0mm i.d. 100mm length, Plowden & Thompson Ltd, UK) were cleaned using the permanganate procedure described above, dried, and then one end was sealed in a Bunsen flame. 125 μm or 25 μm diameter Pt wire (99.99+% Advent Research Materials Ltd, UK) was cleaned by soaking in acidified peroxide solution overnight then electrochemically cleaned in sulphuric acid solution by repeatedly scanning between 0V and 1.2V, stopping at 0V. The dried Pt wire was then inserted into the glass tube, tapped down and then sealed into the glass. Sealing was achieved by attaching the glass tube to a vacuum at its open end and heating in a resistance wire coil, drawing the coil up the tube to soften the glass and cause it to contract

around the platinum wire. After cooling, the protruding Pt wire was connected to a small copper coil soldered to a large copper wire using a small amount of Indium (99.99+% Advent Research Materials Ltd, UK). The electrode was then polished using aluminium oxide polishing paper (Agar Scientific Ltd, UK) of 30 μ m, 9 μ m, 3 μ m, 1 μ m, 0.3 μ m grade sequentially, to expose the Pt disc. Cleaning of the glass tube and platinum wire are crucial in obtaining a good seal, as was obtaining a good vacuum before any heat was applied.

Electrodes were characterised both visually and electrochemically (double layer and CO-oxidation) and rejected if they did not pass any test.

Visual inspection was performed after electrochemical measurements and poor electrodes demonstrated crevassing and destruction of the interface between the Pt and glass.

Electrochemical inspections were performed in 0.5 mol dm⁻³ H₂SO₄. Good electrodes should show no change in the size of the double layer capacitance region after 24 hours soaking in the above electrolyte, indicating minimal creep of solution between the platinum and glass interface. The cyclic voltammogram for the oxidation of a saturated CO_{ads} adlayer; admitted at 450mV, in the absence of dissolved CO should give rise to a sharp single peak between 600mV and 800mV (dependent upon scan rate). The cyclic voltammogram taken immediately after the CO_{ads} oxidation sweep should be identical to that taken in CO-free solution immediately before CO admission and show no behaviour associated with CO_{ads} oxidation.

Unsatisfactory electrodes also typically showed more than one CO_{ads} oxidation peak. It is assumed that during the admission phase some CO diffuses into the stagnant zone within the crevasse formed between the Pt and glass of unsatisfactory electrodes. This reservoir of CO then complicates the electrochemistry and gives rise to extra peaks during the initial oxidation or during the subsequent voltammetric scan.

2.2.3 Achieving uniform access using wall-jet electrodes

Uniform access is important in electrochemical experiments where the diffusion of either reactants to the electrode or products from the electrode can contribute to the overall reaction rate. Uniform access is also important when preparing an adlayer of adsorbed species.

The main issue with the impinging jet approach is associated with the non-uniform access of wall-jet type cell configurations [32]. This occurs because of differences in flow velocities of the fluid as a function of distance from the centre of the jet, and the formation of a central region within which the fluid is virtually stagnant. The net result is that the boundary layer thickness varies as a function of position across the jet. If the electrode is placed axially immediately above the jet, then the effects of non uniform access are exasperated as the boundary layer thickness increases at the central symmetry axis.

In order to assess the extent of non-uniform access, a movable stage was constructed allowing translation of the electrode with a 1µm resolution across the jet. When the electrode is symmetrically placed above the centre of the jet, the limiting current is at a minimum, and the current rapidly rises to a broad maximum before falling away at distances greater than the radius of the impinging jet, Figure 2. It can be seen in Figure 2 that the maximum in the limiting current curve is rather broad.

Also shown in Figure 2 is the variation of boundary layer thickness with displacement from the centre of the jet, calculated from Fick's first law [33] assuming linear diffusion to the electrode, a concentration of zero at the electrode interface and values of the diffusion coefficient and concentration of hydrogen of $3.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [28] and $7.2 \times 10^{-4} \text{ mol dm}^{-3}$ [27] respectively. This curve shows a minimum at the point of maximum current and is quite broad. Indeed, if a 125µm diameter electrode is situated at the centre of this minimum, then the boundary layer thickness varies by no more than 1% from its mean value across the entire face of the electrode. Hence, by positioning the electrode at this physical point, we are confident that the system is operating under acceptable uniform access – a situation which would not exist with electrodes which were significantly larger.

3 Results and discussion

In the following sections the measurement of the charges associated with CO adsorption and oxidation under different conditions are discussed. During CO adsorption and oxidation the nature of the interface may change quite considerably, as described in the introduction, and this may give rise to a number of electrochemical currents, not all of which are due to faradaic processes. Initially, the simplest case where a saturated adlayer is prepared and then oxidised is considered, taking into account each of the different processes which may occur. In the second section this approach is taken one step further to consider the case where only a partial adlayer is formed and oxidised off of the surface.

3.1 Saturated adlayers

CO_{ads} coverages are all calculated relative to the hydrogen desorption and adsorption coverages using the following equation.

Equation 3.
$$\theta_{\text{CO}} = \frac{Q_{\text{CO}_{\text{oxidation}}}}{Q_{\text{H}_{\text{desorption}}} - Q_{\text{H}_{\text{adsorption}}}}$$

$Q_{\text{CO}_{\text{oxidation}}}$ is the CO oxidation charge corrected for all other Faradaic and non faradaic processes.

A typical CO experiment involves (a) Admission: holding the electrode at an admission potential, and dosing the surface with CO; (b) Purging: removing any free CO from solution; (c) Stripping: scanning the potential up until all of the CO_{ads} is oxidised; and (d) either a reverse scan; stepping the potential back down to the admission potential, or a background scan; repeating steps a to c in the absence of CO.

After this complete cycle, the surface is either in the same state as it started, or the same state as the background scan, and the only difference should be that some CO has been oxidised to CO₂, Figure 3.

By measuring and summing the charges associated with each of these processes, it is possible to determine the charge associated with just the CO oxidation process. In the past, this process has been somewhat tedious because of the long delays required to remove all of the CO from solution during step (b). During the admission process, CO adsorbs on the surface, and there may be partial charge transfer, however, for CO admission the electrosorption valency is often assumed to be zero [7], which is the same assumption made here. At the same time, the CO can displace hydrogen (if the adsorption is performed in the hydrogen region), anions (if present), water or any other species adsorbed on the surface. Displacing the adsorbed hydrogen will result in a positive charge. As many anions are partially discharged on adsorption (i.e. they have a non-zero electrosorption valency), their displacement will result in a negative charge for adsorption potentials less than the potential of zero total charge.

Finally there is also charge associated with the change in double layer structure resulting in a decreased capacitance for the electrode.

Equation 6. $Q_{Admission} = Q_{CO_{ads}} + (1-x)Q_{H_{desorption}} - Q_{DoubleLayer} - Q_{AnionAds}$

Where $Q_{CO_{ads}}$ is the charge associated with any charge transfer during the adsorption of the CO. $(1-x)Q_{H_{desorption}}$ is the charge associated with the oxidation of adsorbed hydrogen which has been displaced by the CO_{ads}. 'x' is the proportion of the adsorbed hydrogen which is not displaced by CO_{ads}. $Q_{DoubleLayer}$ is the charge associated with the change in capacitance of the electrode due to CO adsorption. $Q_{AnionAds}$ is the charge association with the adsorption of anions onto the surface (in this case we expect anion desorption, i.e. $Q_{AnionAds}$ is negative).

It is assumed that during the purging process, neither the potential nor the species adsorbed on the electrode change. This may not be true, as either some CO_{ads} oxidation or CO_{ads} desorption may take place, or a relaxation in the compression structure of the CO_{ads} adlayer may take place as the equilibrium between CO_{ads} and CO_{bulk} is changed [18], this is discussed more fully below. For the purposes of calculating coverage it is assumed that no appreciable change in the adlayer will happen over the timescale of the purging, which is nonetheless quite fast for these experiments at about 10s and occurs immediately after the admission process. Experimentally this is seen, and the current measured

is effectively zero over this period. The nature of the experimental procedure means that $Q_{purging}$ is effectively part of the admission process and is therefore can be ignored as a separate step.

During the stripping process CO_{ads} is oxidised and any remaining adsorbed hydrogen is also oxidised. The double layer and adsorbed anions are re-established, and there is growth of oxide. Because of the change in potential, there is some modification to the anion coverage, and the total charge associated with the double layer is also modified ($\Delta Q_{AnionAds}$, $\Delta Q_{DoubleLayer}$ respectively).

Equation 7.

$$Q_{Stripping} = Q_{CO_{oxidation}} - Q_{CO_{ads}} + (x)Q_{H_{desorption}} + Q_{DoubleLayer} + Q_{OxideGrowth} + Q_{AnionAds} + \Delta Q_{DoubleLayer} + \Delta Q_{AnionAds}$$

During the reverse step, the oxide is reduced, hydrogen is adsorbed, and charge is consumed in anion desorption and changes to the double layer structure.

Equation 8.

$$Q_{ReverseStep} = -Q_{H_{desorption}} - Q_{OxideGrowth} - \Delta Q_{DoubleLayer} - \Delta Q_{AnionAds}$$

Or if a background correction is used:

Equation 9.

$$Q_{Background} = Q_{H_{desorption}} + Q_{OxideGrowth} + \Delta Q_{DoubleLayer} + \Delta Q_{AnionAds}$$

Although the background charge is actually made up of a number of background transients $Q_{BackgroundAdmission}$ and $Q_{BackgroundStripping}$ which added together will give $Q_{Background}$. In practice it is usually necessary to correct each step individually, subtracting $Q_{BackgroundAdmission}$ from $Q_{Admission}$ and $Q_{BackgroundStripping}$ from $Q_{Stripping}$. This must be done exceedingly carefully, as discussed below, in particular because some Faradaic processes such as the ORR will occur during the background, but not after CO has been adsorbed.

Charges calculated using Equation 9 or Equation 8 should theoretically be identical but of opposite sign, as in both cases the surface should be entirely free of CO_{ads} and the only difference is in the direction of the potential sweep or step. However, some differences in the amount of oxide growth that has occurred may conceivably occur if the surface examined after the oxidation of CO_{ads} has not had time to equilibrate, and therefore Equation 8 should be more reliable than Equation 9 as this will be independent of whether the system has equilibrated or not. In practice this is also not always the case as other factors complicate the situation, in particular the presence of small amounts of oxygen, which necessitate the use of background transients and Equation 9. This is discussed fully below.

The sum of these four processes represent a complete cycle, with the net difference in charge attributable solely to CO oxidation, therefore the charge attributed solely to the oxidation of CO can be calculated using either of the following equations.

$$\text{Equation 10. } Q_{CO_{oxidation}} = Q_{Admission} + Q_{Stripping} + Q_{ReverseStep}$$

$$\text{Equation 11. } Q_{CO_{oxidation}} = Q_{Admission} + Q_{Stripping} - Q_{BackgroundAdmission} - Q_{BackgroundStripping}$$

An exhaustive analysis of how this is done experimentally is described below.

The typical approach used within the literature [34] to measure CO oxidation charge is to subtract $Q_{ReverseScan}$ (or occasionally $Q_{BackgroundStripping}$) from $Q_{Stripping}$ to produce an indicative CO oxidation charge,

$$\text{Equation 12. } Q'_{CO_{oxidation}} = Q_{Stripping} + Q_{ReverseStep}$$

or,

$$\text{Equation 13. } Q'_{CO_{oxidation}} = Q_{Stripping} - Q_{Background}$$

The relative error associated with this simplification may be estimated as

$$\text{Equation 14. } \text{Error}(CO_{oxidation}) = \frac{Q_{CO_{oxidation}} - Q'_{CO_{oxidation}}}{Q_{CO_{oxidation}}} = \frac{Q_{Admission} + Q_{Purging}}{Q_{Admission} + Q_{Purging} + Q_{Stripping} + Q_{ReverseStep}}$$

It is useful to assess this error in terms of describing the absolute charge associated with the oxidation of CO_{ads} .

3.1.1 CO admission phase

The chronoamperometric transients in Figure 4(a) show the effect of switching from Reservoir 2 (N_2 saturated CO-free H_2SO_4) to Reservoir 1 (CO saturated H_2SO_4) about 20s after the transient starts. For comparison, the case when both reservoirs 1&2 are filled with N_2 saturated CO-free H_2SO_4 is also shown (grey transient). In this latter case a transient is seen which takes almost 300s to stabilise. This long-time cathodic current, in absolute terms only 0.66nA ($1.7\mu A cm^{-2}$), is associated with the presence of a small amount of residual oxygen in the electrolyte as described above. The initial decay is associated with residual oxygen diffusing through the ptfе valve body. The flux of oxygen into the electrolyte decreases with time as the reservoir of oxygen dissolved in the ptfе is consumed. It must be stressed that the amount of oxygen is very small, $\sim 45 \times 10^{-9} \text{ mol dm}^{-3}$, and it is an indication of the sensitivity of these experiments that it can be detected.

When the second electrolyte contains CO (Figure 4(a) black line), the transient is initially the same until about 35s when the CO containing electrolyte starts bathing the electrode. As soon as the CO containing solution bathes the electrode there is an immediate anodic peak due to the oxidation of adsorbed hydrogen as it is displaced by the adsorbed CO, Equation 4. This peak decays very quickly and is replaced by a much slower cathodic transient as anion desorption becomes significant, Equation

5. Once a CO_{ads} monolayer has been formed the *ORR* current is effectively suppressed as the CO_{ads} monolayer blocks the adsorption of O_2 and hence stops the *ORR* reaction.

In order to calculate the charge due to the admission of CO alone it is necessary to correct for the effect of the *ORR*. This is complicated by the fact that the *ORR* is suppressed during CO adsorption. A subtraction of the transient when no CO is admitted (grey line, Figure 4 (a)) from the transient when CO is admitted is shown in Figure 4(b). It is clear from this transient that it is possible to remove any charge contributions from processes occurring before the CO admission takes place. However, at long time this transient does not decay to zero, but shows a positive current because of the suppression of the *ORR* on the CO covered surface.

To overcome this effect we construct a non-constant baseline for the integration as shown in Figure 4(b). This baseline is an extrapolation of the transient before CO admission takes place and at long time after CO admission has taken place, with a transition between the two baselines at the exact moment of the peak current. This is based upon the assumption that the *ORR* current will decrease linearly with increasing CO_{ads} coverage, and that the CO adsorption/displacement peak is symmetrical.

3.1.2 CO_{ads} oxidation phase

Figure 5(a) shows the current measured during the CO_{ads} oxidation phase. There is an initial large spike which has been attributed to the removal of upd hydrogen and double layer charging which is larger for the control surface which has no CO_{ads} present, and this decays away rapidly. For the surface with CO_{ads} present there is significant oxidative current after approximately 1s, with a pronounced asymmetric peak, peaking at approximately 2.5s and with the current decaying away to that seen for the control after approximately 20s.

In order to correctly determine the charge associated with oxidising the CO_{ads} on the surface it is necessary to subtract the control transient from the transient for which CO_{ads} is present. This is shown in Figure 5(b). Note that initially there is a negative current. This is associated with the removal of the upd hydrogen from the control surface, for which the charge is far greater than the removal of the remaining upd hydrogen on the surface covered with CO_{ads} . After this initial negative current the current becomes positive as the current associated with CO_{ads} oxidation starts to increase rapidly, and the current then decays away to zero as the surface becomes identical to that of the control. All of the charges here must be included, as the initial negative current due to removal of upd hydrogen from the control was instead passed during the CO admission process and therefore must be taken into account here.

The integration of the charge passed throughout the CO_{ads} oxidation process minus the control is shown in Figure 5(c).

The maximum in charge is reached after approximately 30s, the integrated charge then starts to decay away, although the rate of decay decreases over time. The cause of this is unknown, but it is

possible that this is again caused by the *ORR*, although the magnitude of the current is far less. However, it is possible to reduce the effect of the discrepancy by taking the maximum charge passed.

The total charge passed throughout this experiment without correcting for the unknown decay was 66.4nC, and including the corrections was 72.7nC. The error without corrections is -8.6%, equivalent to an underestimation of the CO_{ads} coverage by 0.038, or 5.7%.

3.1.3 Returning to the admission potential

It is expected that the chronoamperometric transients for returning to the admission potential for both the background and the oxidation experiments should be identical, as the surfaces should now be in the same state.

This is broadly the case; the difference in charge passed between the CO_{ads} oxidation experiment and the background shown was only 0.77nC, which is equivalent to a CO_{ads} coverage of 0.0039, or 0.67% of the saturated CO_{ads} adlayer. Therefore, we assume that the difference between these two charges is experimental error and it is not necessary to include this charge in the coverage calculations.

3.1.4 Coverage calculations

The CO_{ads} coverages for five independent experiments with independent background experiments, calculated using Equation 10 are shown in Table 1.

A standard deviation of 1.17% from 5 experiments was considered to be acceptable, and the value of 0.68 is in agreement with similar experiments in the literature for Pt(111) electrodes, for which the maximum coverage in CO free 0.1 mol dm⁻³ H₂SO₄ was shown to be 0.68 [18]. If the coverage had been calculated only from the stripping charge with a background correction, then the coverage would have been calculated as 0.444, an underestimation of 34% as calculated by Equation 14. The error is associated with the extra charge associated with anion adsorption, and so is expected to be potential dependent. It is expected that the error would reduce to zero if the CO adsorption were done at the potential of zero total charge.

3.2 Sub-saturated adlayers – Partial Admission

There are two approaches to produce sub-saturated CO_{ads} adlayers on Pt, the first called partial admission involves exposing the Pt electrode to CO saturated solution for controlled periods of time below that needed to obtain a saturated adlayer, and the second called partial oxidation involves exposing the Pt electrode to CO saturated solution until a saturated adlayer is achieved and then partially oxidising the CO_{ads} adlayer. In a separate paper we will compare the activity of Pt electrodes towards the hydrogen oxidation reaction with different partial CO coverages prepared by these two different methods.

Partial admission is the most difficult approach to prepare sub-saturated CO_{ads} adlayer as in normal electrochemical cells it is difficult to control the exposure of the electrode to the CO saturated electrolyte. Therefore it has only really been studied in the past by Bergelin et al. [17, 35] who used an impinging jet to control the solution flowing over the electrode. As mentioned above we have used the same approach here with some improvements to ensure that there is uniform access of CO to the electrode surface during the partial admission approach in order to achieve a uniform coverage of CO_{ads} across the electrode surface.

Equation 10 can be used for calculating the CO_{ads} coverage for saturated and non-saturated CO adlayers produced by controlling the admission time. In effect, the method for calculating the CO_{ads} coverage is exactly the same as described above, the only difference is that the amount of CO_{ads} on the surface is less than a full saturated layer as the CO exposure time is shorter than that required to produce such a layer.

Figure 6 displays the coverage of CO_{ads} measured as a function of the amount of time that the electrode is exposed to the CO containing solution. Each point corresponds to a separate adsorption/oxidation experiment. Within about 1 s the electrode becomes saturated with CO_{ads} . Further increasing the exposure does not lead to any significant change in CO_{ads} coverage. CO adsorption on the Pt surface requires transport from the bulk (CO_{bulk}) to the area immediately adjacent to the electrode (CO_{surf}) and then from there onto the surface (CO_{ads})

Where k_{mt} represents the mass transport rate constant of the CO to the immediately adjacent to the surface and k_{ads} represents the adsorption rate constant of the CO onto the surface. When $k_{mt} \gg k_{ads}$ then the CO_{ads} surface concentration (c_{surf}) is the same as the bulk concentration (c_{bulk}) and the rate of adsorption is dominated by k_{ads} . If $k_{mt} \approx k_{ads}$ then the surface concentration of CO_{ads} will be less than the bulk concentration, and it will be necessary to consider both transport steps in order to determine k_{ads} . Finally, when $k_{ads} \gg k_{mt}$, mass transport to the surface is the limiting step, the CO_{ads} surface concentration is close to 0 and it is difficult to obtain accurate values of k_{ads} in any experiment.

As we are under uniform access conditions, and the boundary layer thickness is constant across the electrode, mass transport to the electrode is determined by diffusion through the boundary layer, which is strongly convected on its external boundary. Hence

Equation 16. $k_{mt} = \frac{D_{CO}}{\delta}$

Where δ is the width of the boundary layer, and D_{CO} is the diffusion coefficient of CO in solution. In our experiments the boundary layer thickness is $\sim 4.6\mu m$ (Figure 2, this paper) and utilising a CO diffusion coefficient $1.46 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [36] we obtain a value of k_{mt} of 0.0317 cm s^{-1} . Because of the

controlled geometry of our experiment, and the fact that the boundary layer thickness is uniform, we can determine the flux of reactant to the surface layer using Ficks' first law

$$\text{Equation 17. } J_{mt} = D_{CO} \left(\frac{c_{bulk} - c_{surf}}{\delta} \right) = k_{mt} (c_{bulk} - c_{surf})$$

The adsorption of CO onto platinum (second step in equation 15) in the simplest case may be considered to follow a Langmuir adsorption isotherm in which the CO_{ads} adsorbed on the surface is in equilibrium with CO immediately adjacent to the surface. Hence in the ideal case we also need to include the desorption rate constant for CO_{ads} from the surface. However, at the temperature of the experiments performed in this paper k_{des} is exceedingly small, and CO adsorption is effectively irreversible (this will be shown later in the paper). Hence we set $k_{des}=0$.

The rate of change of CO_{ads} surface coverage with time for this situation may be written as

$$\text{Equation 19. } \frac{d\theta}{dt} = k_{ads} c_{surf} (1 - \theta) - k_{des} \theta = k_{ads} c_{surf} (1 - \theta)$$

This ignores any interaction between the adsorbed CO_{ads} molecules, which could be modelled using a Frumkin-type correction factor, but which for simplicity we have not done. We can also ascribe a flux of CO due to this absorption process to the surface

$$\text{Equation 20. } J_{ads} = \frac{1}{N_{0,CO}} \frac{d\theta}{dt} = \frac{k_{ads}}{N_{0,CO}} c_{surf} (1 - \theta)$$

Where $N_{0,CO}$ is the number of surface sites on the Pt surface available to adsorb CO (i.e. $\theta_{CO,max} N_0$, where $\theta_{CO,max}$ the maximum CO_{ads} coverage is taken to be 0.68). As the two fluxes must be equal, we can equate Equation 17 and Equation 20 and solve for c_{surf} . Substituting the resulting expression for c_{surf} into Equation 19 and rearranging provides an equation for the change in surface coverage of CO_{ads} as a function of time under the conditions of our experiment

$$\text{Equation 21. } \frac{d\theta}{dt} = \frac{k_{ads} k_{mt} c_{bulk} (1 - \theta)}{N_{0,CO} (k_{ads} \theta - k_{mt} - k_{ads})}$$

The solution of this differential equation is found and incorporates the Lambert W-Function (this function is the inverse function of $f(W) = We^W$),

$$\text{Equation 22. } \theta[t] = 1 - \frac{k_{mt}}{k_{ads}} W \left[-\frac{k_{ads}}{k_{mt}} \text{Exp} \left[\frac{k_{ads} - \text{const}}{k_{mt}} - \frac{k_{ads} c_{bulk} t}{N_{0,CO}} \right] \right]$$

Where $const$ is the constant of integration. The value of this is determined by solving Equation 19 for $const$ under the boundary condition $\theta_{t=0} = 0$. This leads to

$$\text{Equation 23. } \theta[t] = 1 - \frac{k_{mt}}{k_{ads}} \text{W} \left[\frac{k_{ads}}{k_{mt}} \text{Exp} \left[\frac{k_{ads}}{k_{mt}} - \frac{k_{ads} C_{bulk} t}{N_{0,CO}} \right] \right]$$

This equation was used to fit the data in Figure 6 utilising k_{ads} as the only fit parameter. The values of the other constants are listed previously and the CO solubility used was $0.96 \times 10^{-6} \text{ mol cm}^3$ [37]. The nonlinear fit was performed in Mathematica, and resulting best fit value of k_{ads} is 0.0086 cm s^{-1} . This value is within a factor two of the value calculated at 298 K from the data in Baschuk and Li [38], 0.015 cm s^{-1} . The error bars shown in Figure 6 reflect the average differences in the coverages calculated using Equation 10 and Equation 11.

From this result we also see that $k_{mt} \approx 4 \times k_{ads}$ suggesting that these experiments are operating in the intermediate regime where the overall rate of adsorption is controlled by both transport from bulk solution and the actual adsorption process. This confirms the need to take both processes into account within the mathematical derivation.

3.3 Sub-saturated adlayers – Partial Oxidation

The partial oxidation process involves the formation of a saturated CO_{ads} adlayer followed by the removal of some of that adlayer by oxidation. In order to determine the CO_{ads} coverage of the resultant layer, we need to assess not only the saturated CO_{ads} coverage, but also assess how much of the CO_{ads} has been oxidised during the electrochemical oxidation process.

Figure 7 shows a cartoon of the potential steps applied to the system and the current responses expected when CO is adsorbed on the electrode during the admission stage (CO oxidation transient) and when no CO is adsorbed (Control transient). The crucial parameter is t_{strip} which represents the amount of time that the electrode with a saturated CO_{ads} adlayer is oxidised for. During phase (d), other experiments can be performed to probe the nature of the adsorbed layer, although in this paper we have not done so.

Figure 8 shows experimental results for two different values of t_{strip} , 0.1 and 3 s. Reassuringly there is no difference in the transients during the admission phase of the experiment, Figure 8(a). For comparison to these admission transients, Figure 8(b) shows the transient when no CO is present in the solution during the admission phase. There is a limiting cathodic current plateau when no CO is adsorbed. This limiting current is much smaller when a saturated CO_{ads} adlayer is formed. Figure 8(c) shows the transient for the partial oxidation of the CO_{ads} adlayer. Both transients overlay each other until 0.1 s into the transient at which point the potential is switched back to 100 mV for the $t_{strip}=0.1\text{s}$ transients, and a small cathodic reverse transient is seen. That reverse transient is replotted in Figure

8(d) and overlaid with the equivalent reverse step transient for the $t_{strip}=3s$ oxidation experiment. It can be seen that the charge associated with the shorter t_{strip} is smaller, as the surface is still substantially covered with CO_{ads} , which will reduce the double-layer capacitance and coverage of adsorbed anions. The situation is reversed for the second stripping phase, Figure 8(e). In this transient the $t_{strip}=0.1s$ oxidation experiment shows a larger transient as there is a larger amount of unreacted CO_{ads} on the electrode surface. The second reverse steps, Figure 8(f) are identical for the different experiments.

In analysing the charges associated with each of these different transients, we need to modify some of the equations which we previously used for the complete oxidation case. Equation 6 and Equation 8 remain the same, however instead of Equation 7 there are now two oxidation steps and two reverse steps.

$$\text{Equation 24. } Q'_{stripping} = (m)Q_{CO_{oxidation}} - (m)Q_{CO_{ads}} + (x)Q_{H_{desorption}} + (a)Q_{DoubleLayer} + (a)Q_{AnionAds} + Q'_{OxideGrowth} + \Delta Q'_{DoubleLayer} + \Delta Q'_{AnionAds}$$

$$\text{Equation 25. } Q'_{ReverseStep} = -(z)Q_{H_{desorption}} - Q'_{OxideGrowth} - \Delta Q'_{DoubleLayer} - \Delta Q'_{AnionAds}$$

$$\text{Equation 26. } Q''_{stripping} = (1-m)Q_{CO_{oxidation}} - (1-m)Q_{CO_{ads}} + (z)Q_{H_{desorption}} + (1-a)Q_{DoubleLayer} + (1-a)Q_{AnionAds} + Q''_{OxideGrowth} + \Delta Q''_{DoubleLayer} + \Delta Q''_{AnionAds}$$

$$\text{Equation 27. } Q''_{ReverseStep} = -Q_{H_{desorption}} - Q''_{OxideGrowth} - \Delta Q''_{DoubleLayer} - \Delta Q''_{AnionAds}$$

Where 'm' represents the proportion of CO_{ads} oxidised during the first partial oxidation step; and 'a' represents the proportion of anion adsorption and double layer charge associated with the loss of the proportion 'm' of CO_{ads} coverage. 'x' is the same as before but 'z' is an unknown quantity and represents an amount of H_{ads} that forms during the first reverse step and is then oxidised during the second (full) oxidation step.

By summing the oxidation step with the reverse step we get the following:

$$\text{Equation 28. } Q'_{stripping} + Q'_{ReverseStep} = (m)Q_{CO_{oxidation}} - (m)Q_{CO_{ads}} + (a)Q_{DoubleLayer} + (a)Q_{AnionAds} + (x-z)Q_{H_{desorption}}$$

$$\text{Equation 29. } Q''_{stripping} + Q''_{ReverseStep} = (1-m)Q_{CO_{oxidation}} - (1-m)Q_{CO_{ads}} + (1-a)Q_{DoubleLayer} + (1-a)Q_{AnionAds} - (1-z)Q_{H_{desorption}}$$

'z' is clearly a complicating factor and unfortunately it is not possible to measure 'z' directly using these experiments, and thus it has to be assumed that the proportion of H_{ads} that forms during the first reverse step is proportional to the amount of CO_{ads} oxidised during the first partial oxidation step, as shown in Equation 30. The additional difficulty at this stage is that there is only one admission charge

$Q_{\text{Admission}}$ which contains the following terms; $Q_{\text{CO}_{\text{ads}}}$, $(1-x)Q_{\text{H}_{\text{desorption}}}$, $Q_{\text{DoubleLayer}}$, and Q_{AnionAds} . It is therefore necessary to make the further assumption that the electrosorption valencies are independent of coverage, and that no reorganization of the CO_{ads} adlayer occurs. Furthermore we assume that changes to the double layer capacitance and coverage of anions vary linearly with CO_{ads} coverage. Under these assumptions, the ratio of total charge passed during the two oxidation steps is equal to the ratios of CO_{ads} oxidation, hydrogen desorption, double layer reformation and anion adsorption occurring during the oxidation and reverse steps as follows.

$$\text{Equation 30. } \frac{Q'_{\text{stripping}} + Q'_{\text{ReverseStep}}}{Q''_{\text{stripping}} + Q''_{\text{ReverseStep}}} = \frac{m}{(1-m)} = \frac{a}{(1-a)} = \frac{z}{(1-x)}$$

This appears to be the most reasonable approximation possible using our experimental approach. At intermediate coverages there will be some deviation due to adsorbate-adsorbate interactions and/or reorganisation of the CO_{ads} adlayer during CO_{ads} oxidation, as confirmed by experiments showing that hydrogen adsorption can be completely blocked at coverages below the maximum [39]. However it has not been possible to compensate for these effects as they are relatively poorly understood for this system. This will be explored in a future paper. Therefore the coverage must be calculated as follows.

$$\text{Equation 31. } Q'_{\text{CO}_{\text{oxidation}}} = Q'_{\text{stripping}} + Q'_{\text{Reverse}} + \left(\frac{Q'_{\text{stripping+Reverse}}}{Q'_{\text{stripping+Reverse}} + Q''_{\text{stripping+Reverse}}} \right) Q_{\text{Admission}}$$

and,

$$\text{Equation 32. } Q''_{\text{CO}_{\text{oxidation}}} = Q''_{\text{stripping}} + Q''_{\text{Reverse}} + \left(\frac{Q''_{\text{stripping+Reverse}}}{Q'_{\text{stripping+Reverse}} + Q''_{\text{stripping+Reverse}}} \right) Q_{\text{Admission}}$$

The charges from the above equations can then be converted to coverages utilising Equation 3.

The coverages calculated for typical sub-saturated CO_{ads} adlayers prepared by partial oxidation are shown in Figure 9 as a function of t_{strip} . The derivative of this has the same form as the transient for the oxidation of a saturated CO_{ads} adlayer shown in Figure 8 (c) as would be expected. Each point represents an individual stripping experiment. The CO coverage quickly approaches 0 within about 1 s, but shows an extended tail. Indeed, the coverages seem to follow a sigmoidal variation with the logarithm of stripping time, Figure 9 inset. Clearly the shape of this curve holds important information about the mechanism for CO oxidation on our platinum electrode, but we will not analyse this data any more in this paper.

Also displayed in Figure 9 is the total CO coverage for each stripping experiment, calculated using the sum of Q'_{CO} and Q''_{CO} . By inspection of the chrono-amperometric transients it is known that the

oxidation is entirely complete by 3s, therefore the coverage at 3s shown in Figure 9 appears slightly too high, and there appears to be a systematic error which overestimates the CO_{ads} coverage at long time. This error seems too high, and therefore there must be some discrepancy in the charges calculated. Such an effect is also seen for the total coverage, for which the points at 2s & 3s appear to be too high. This is thought to be because of errors in the correction for the charge associated with the *ORR* in the potential step returning to the admission potential, as discussed earlier.

3.4 The effect of purging time

As discussed above, for the purposes of calculating coverage it is assumed that no appreciable change in the adlayer will happen over the timescale of the purging (phase (b) in Figure 7), and therefore the charge due to purging will be zero. The purging time is defined as the delay between the admission of the CO and the oxidation of the CO_{ads} . During the admission phase of the experiment, upon switching between electrolyte containing dissolved CO and electrolyte containing dissolved N_2 , there was no measurable current. In contrast Lopez-Cudero et al [18] showed that on Pt(111) a maximum coverage of $\theta_{\text{CO}} = 0.75$ is achievable in CO saturated solution, but in CO free solution a coverage of $\theta_{\text{CO}} = 0.68$ - 0.69 is achievable, and it can take up to 1 hour for the CO_{ads} adlayer to equilibrate to the lower coverage via desorption once degassing commences.

Experiments conducted with an increasing time delay between the admission and oxidation phases of the experiment showed no appreciable effect upon the CO coverage with time present in Figure 10. The rate of loss of CO from the surface calculated using a linear regression line is $0.32\% \text{ Hour}^{-1}$ with an error of $0.94\% \text{ Hour}^{-1}$, giving a maximum possible rate of loss of $1.27\% \text{ Hour}^{-1}$. This can be used to set an upper limit on k_{des} (equation 18) of $5.3 \times 10^{-6} \text{ s}^{-1}$, more than 1000-fold smaller than k_{ads} . This implies that the CO_{ads} is very strongly adsorbed upon the surface and does not appreciably desorb in the absence of CO in solution at the temperatures of these experiments (25°C). This also justifies the simplification used in Equation 19 in ignoring the desorption reaction. The very slow rate of CO loss also implies that the heterogeneous reaction between molecular oxygen and adsorbed CO is very slow under the conditions used within this experiment. This also suggests that the presence of trace amounts of O_2 as discussed above, are not reacting directly with the CO_{ads} and removing it from the surface.

It is therefore possible to conclude that either it is not possible to achieve a maximum coverage of $\theta_{\text{CO}} = 0.75$ in CO saturated solution for polycrystalline Pt, or that the subsequent desorption process is so fast after switching to CO free solution that it is not possible to measure it. It appears likely that the former is correct which would be in agreement with Rodes et al. who showed that the formation of compressed structures ($\theta_{\text{CO}} = 0.75$) is linked to ‘perfect’ single crystal surfaces, and they are not achievable on polycrystalline surfaces [40]. Either way it is reasonable to assume that once prepared the coverage of the CO_{ads} adlayers is stable over the timescales of our experiments.

4 Conclusions

Calculating the coverage of a CO_{ads} adlayer using electrochemical measurements can be done accurately and reliably. However, it is not easy, and the charge passed during both admission and oxidation, and either a background or a return to the admission potential must be considered. In addition the presence of CO_{ads} may affect any other charge transfer processes that occur, for example the *ORR*, and even very low concentrations of species such as O_2 can seriously affect the results. It is possible to compensate for complications like this, but it must be done very carefully and rigorously. Failure to properly compensate for hydrogen adsorption/desorption, anion adsorption/desorption and double layer effects may lead to an over or underestimation of CO_{ads} coverage dependent upon admission potential. At an admission potential of 100mV this error was calculated to be an underestimation of 34%. This error is related to the admission potential. As the extent of anion adsorption decreases, the error would also decrease. At the potential of zero total charge, the error would be expected to be zero.

The adsorption rate constant for CO on platinum in sulphuric acid at 25°C is calculated to be 0.0086 cm s^{-1} . It appears that the presence of O_2 at the concentration estimated here of $4.5 \times 10^{-8} \text{ mol dm}^{-3}$ does not react noticeably with CO_{ads} in a saturated adlayer, and the CO_{ads} adlayers are stable for over 1½ hours or more.

Calculating the coverage of a partial CO_{ads} adlayer prepared via partial oxidation is even more difficult and must be done relative to a known charge for a complete CO_{ads} adlayer and a background transient prepared under identical conditions. It is not possible to compensate for any changes in the CO_{ads} adlayer between the first and second oxidation steps, although it is likely these occur. Therefore, there are limitations to the accuracy of the coverages calculated for partial adlayers and the errors are likely to be significant at low coverages.

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Figure Captions

Figure 1. Cartoon depicting the impinging jet flow cell apparatus, (a). The flow rate was approximately $6 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$, the capillary tube internal diameter was 0.53mm, the electrode diameter 125 μm , and the distance from the capillary tube to the electrode approximately 2mm. (b) shows a close-up of the working electrode. The counter and reference electrodes are both in the bulk solution and are in electrochemical contact with the working electrode through the meniscus, flow rate through the meniscus is faster than diffusion removing reaction products and preventing contamination of the electrode surface from the bulk.

Figure 2. Diffusion limiting current (calculated using geometric surface area) for hydrogen oxidation at a potential of 100mV on a 25 μm diameter polycrystalline Pt electrode (3000 μm diameter glass sheath surrounding electrode) in a jet of solution containing H_2 saturated 0.5 mol dm^{-3} H_2SO_4 ($\square$). The calculated boundary layer thickness as the electrode is translated from immediately above the centre of the jet (530 μm internal diameter) radially is shown (dashed line). The zero point on the horizontal scale corresponds to the electrode being positioned coaxially with the jet (i.e. the same configuration as shown in Figure 1(b)).

Figure 3. Cartoon showing the potential steps and current transients associated with the preparation and complete oxidation of a CO_{ads} adlayer, and for the control case when no CO is adsorbed on the surface. The only difference between the two experiments is that during the admission phase (b) CO is present in the solution for the first case, and not for the control experiment.

Figure 4. Chronoamperometric transients at a potential of 100mV in N_2 -saturated 0.5 mol dm^{-3} H_2SO_4 for the admission of a CO-saturated 0.5 mol dm^{-3} H_2SO_4 for 60s after a delay of roughly 35s (black line), and a control where no CO-saturated solution is admitted to the surface (grey line), (a). Subtraction of the control chrono-amperometric transient from the chrono-amperometric transient where CO is admitted to the surface, (b). Baseline for integration of this transient is also shown (.....).

Figure 5. Chrono-amperometric transients at a potential of 700mV in N_2 -saturated 0.5 mol dm^{-3} H_2SO_4 for the oxidation of a CO_{ads} adlayer prepared by admission of CO-saturated 0.5 mol dm^{-3} H_2SO_4 for a period of 60s at 100mV (black line), and a control for a surface with no CO present but which has undergone the same potential regime (grey line) (a). Followed by subtraction of the control transient from the CO_{ads} oxidation transient (b). And finally, the integration of the current passed after subtraction of the control transient (c).

Figure 6. CO coverage for a polycrystalline Pt electrode in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ of CO_{ads} adlayers produced by exposing the electrode to bursts of CO-saturated 0.5 mol dm⁻³ H₂SO₄ for various lengths of time. Admission potentials of 67 mV.

Figure 7. Cartoon showing the potential steps and current transients associated with the preparation of a partial CO_{ads} adlayer by partially oxidising a saturated adlayer for a period of t_{strip}. This then followed by a complete oxidation of the remaining layer.

Figure 8. Chrono-amperometric transients at a potential of 100mV in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ for the admission of CO-saturated 0.5 mol dm⁻³ H₂SO₄ for a period of 10s (a), compared to the background transient (b). Followed by the transients in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ for the oxidation of the CO_{ads} adlayer at 700mV for 0.1s (- - -) and 3s (—) (c), and the return step to 100mV (d). And finally, the transients in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ for the oxidation of the remaining CO_{ads} at 800mV for 10s (e), and the return step to 100mV (f).

Figure 9. CO_{ads} coverages remaining after partial oxidation for CO_{ads} adlayers prepared by admission of CO from CO-saturated 0.5 mol dm⁻³ H₂SO₄ at a potential of 100mV for 10s, followed by partial oxidation in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ at a potential of 800mV for lengths of time between 0.005s and 3s, □. Following the formation of the partial CO adlayer, the remaining CO was completely oxidised at a potential of 800mV for 10s. The coverage was calculated using the corrected oxidation charges, Equation 31&32. The total CO coverage obtained from $Q'_{CO_{oxidation}} + Q''_{CO_{oxidation}}$ is also plotted, (O). Inset shows the same data represented with a semi-logarithmic plot.

Figure 10. CO_{ads} coverages after partial oxidation for CO_{ads} adlayers prepared by admission of CO from CO-saturated 0.5 mol dm⁻³ H₂SO₄ at a potential of 100mV for 10s, followed by partial oxidation in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ at a CO_{ads} coverages remaining after saturated CO adlayers (prepared by admission from CO-saturated 0.5 mol dm⁻³ H₂SO₄ at a potential of 100 mV for 60 s) were held at potentials of 100mV in N₂-saturated 0.5 mol dm⁻³ H₂SO₄ for different lengths of time.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Table 1 Charge consumed by each of the two major steps associated with CO oxidation – admission and stripping. The errors associated with calculating these charges and the resulting CO coverage. Errors are calculated from the statistical analysis of five experiments.

	Charges / nC		
	Mean	Standard Deviation (SD)	Error (SD/Mean)
$Q_{\text{Admission}} - Q_{\text{BackgroundAdmission}}$	37.3	1.146	3.07%
$Q_{\text{Stripping}} - Q_{\text{BackgroundStripping}}$	71.2	1.689	1.51%
$Q_{\text{CO}_{\text{oxidation}}}$	108.5	1.26	0.82%
Coverage (θ_{CO})	0.676	0.008	1.17%