

# Identification of CO Adsorbed at Ru and Pt Sites on a Polycrystalline Pt/Ru Electrode and the Observation of Their Oxidation and Free Interchange under Open Circuit Conditions

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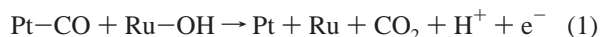
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The spontaneous oxidation of CO adsorbates on a Pt electrode modified by Ru under open circuit (OC) conditions in perchloric acid solution has been followed, for the first time, using in situ FTIR spectroscopy, and the dynamics of the surface processes taking place have been elucidated. The IR data show that adsorbed CO present on both the Ru and Pt domains and can be oxidized by the oxygen-containing adlayer on the Ru in a chemical process to produce CO<sub>2</sub> under OC conditions. There is a free exchange of CO<sub>ads</sub> between the Ru and Pt sites. Oxidation of CO<sub>ads</sub> may take place at the edges of the Ru islands, but CO<sub>ads</sub> transfer, at least on the time scale of these experiments, allows the two different populations to maintain equilibrium. Oxidation is limited in this region by the rate of supply of oxygen to the surface of the catalyst. A mechanism is postulated to explain the observed behavior.

## Introduction

Despite a wealth of literature on the subject, the mechanism by which Ru promotes the oxidation of CO at Pt based fuel cell electrocatalysts remains controversial and this controversy has been highlighted recently by experiments on the stripping voltammetry of CO adsorbed at Pt(111) and Ru/Pt(111).<sup>1–5</sup> There seems to be general agreement that the two peaks observed in the CO-stripping experiment may be attributed to the removal of adsorbed CO present in two well-defined zones, but controversy surrounds the identification of these zones: Zone 1 is the Pt atoms immediately adjacent to the Ru islands<sup>1,2</sup> (Pt\*) or these sites *and* Ru islands themselves<sup>4,6,7</sup> and zone 2 comprises either sites one or more atoms away from the Pt\* sites<sup>1,2</sup> or the Pt\* sites but with the stripping peak attributed to the slow diffusion of adsorbed CO to the Pt\* sites from the Pt atoms further away from the Ru islands.<sup>4,6,7</sup> Electrolyte adsorption also appears to be an important factor.<sup>1,2</sup>

The work of Hayden and colleagues<sup>1,2</sup> supports the bifunctional mechanism of Watanabe and Motoo<sup>3</sup> in which the Ru supplies active oxygen at lower potentials than is possible at Pt alone via a Langmuir–Hinshelwood mechanism:

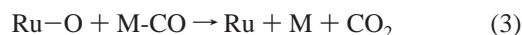
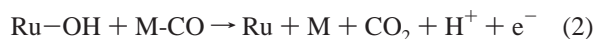


According to Hayden, zone 1 comprises the Pt\* sites and zone 2 comprises the Pt sites one or more atoms away from the Pt\* edge atoms. This model allows for no role at all for CO adsorbed on the Ru islands, these domains simply act as a reservoir of active OH species; this aspect of the model is supported by emersion studies where a monotonic reduction in the coverage of Pt(111) by adsorbed CO was observed on increasing the coverage of the Pt surface by Ru.<sup>1,2</sup> However, our results presented below suggest that this latter observations may be

explained in terms of the chemical reaction of adsorbed OH/oxygen in solution (present at c. 10<sup>-5</sup> M) and CO<sub>ads</sub> species during the emersion process. Both Koper and colleagues<sup>7–9</sup> and Wieckowski and co-workers<sup>4,6</sup> disagree with Hayden as to the possible role of CO adsorbed on the Ru islands. Koper<sup>7</sup> suggests that zone 1 consists of CO adsorbed at both the edge Pt\* sites around the Ru islands, and on the Ru islands themselves, and offers the possibility that the CO adsorbed at the Ru sites with adjacent Ru–OH species may be oxidized faster than that adsorbed at the Pt\* sites reacting with adjacent Ru–OH species. Koper et al. postulate that the second stripping peak is due to the slow diffusion of CO<sub>ads</sub> from the “normal” Pt(111) sites to active Pt\* sites freed up by oxidation during the first stripping process. No significant oxidation of adsorbed CO takes place away from the Pt\* and Ru sites. Wieckowski and co-workers<sup>4,6</sup> formulate a model very similar to that of Koper et al. Wieckowski<sup>10</sup> has suggested that the CO stripping experiments detailed above may stimulate a significant shift in the understanding of the promotional activity of Ru.

For the first time since the original work of Watanabe and Motoo,<sup>3</sup> CO adsorption and oxidation at the Ru domains of Ru/Pt electrodes is being postulated<sup>4,6–9</sup> and, indeed, this may be a significant route to CO<sub>2</sub>,<sup>4,7</sup> all of which is in line with our own studies on the adsorption and oxidation of CO and other small organic molecules at well-defined Ru(0001) electrodes.<sup>11–15</sup> Clearly, significant interest is focusing on the diffusion of adsorbed CO across the Pt surface, and the role of anion adsorption upon this process; however, no one has postulated the free exchange of CO<sub>ads</sub> between the Pt and Ru domains.

In broad terms, there are three likely mechanisms for the oxidation of adsorbed CO:



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where  $M = \text{Ru}$  or  $\text{Pt}$ . The processes shown as equations 3 and 4 were postulated by Watanabe and Motoo<sup>3</sup> on the basis of simple open circuit potential (OCP) measurements in 1975 (along with an analogous process at  $\text{Pt}$ ), but this appears to have dropped out of thinking in this area since, and so reactions 3 and 4 are not generally considered; to this end, this paper reports new molecular data on the oxidation of adsorbed  $\text{CO}$  at  $\text{Ru}$  and  $\text{Pt}$  sites on  $\text{Ru}$ -polycrystalline  $\text{Pt}$  electrodes in perchloric acid electrolyte under open circuit conditions, which allow the observation of the free interchange of the adsorbed  $\text{CO}$  between the two sites.

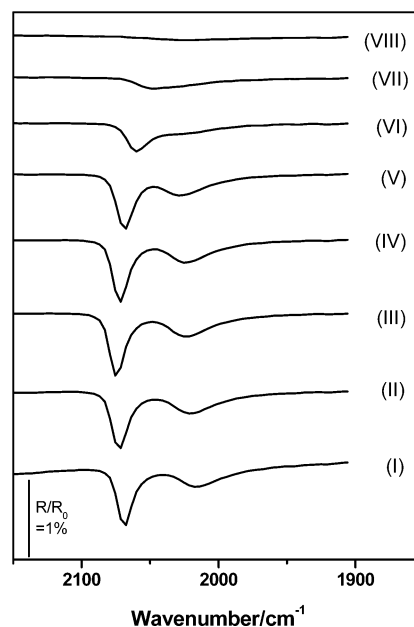
## Experimental Section

The working electrode was a polycrystalline  $\text{Pt}$  "top hat"-shaped electrode ( $\text{pc-Pt}$ ) with an area of  $0.64 \text{ cm}^2$  exposed to the electrolyte. The  $\text{Ru}_{\text{ad}}/\text{Pt}$  electrode was prepared by the spontaneous deposition of  $\text{Ru}$  onto the  $\text{pc-Pt}$  electrode from a solution of  $0.2 \text{ M RuCl}_3/0.1 \text{ M HClO}_4$  for 1 min; the coverage of  $\text{Ru}$  was determined according to the method of Watanabe and Motoo<sup>3</sup> and found to be *c.* 0.3. All potentials are given vs the  $\text{Ag}/\text{AgCl}$  electrode in saturated  $\text{KCl}$  solution. Details of the in situ FTIR experiments can be found elsewhere.<sup>11–15</sup> The reflectance spectra presented below consist of 64 co-added and averaged scans ( $8 \text{ cm}^{-1}$  resolution, *ca.* 16 s per scanset) unless stated otherwise and are calculated as the ratio  $(R/R_0)$  vs  $\nu/\text{cm}^{-1}$ , where  $R_0$  is the reference spectrum and  $R$  the spectra collected as a function of potential or time. These data manipulation results in spectra in which peaks pointing up, to  $+(R/R_0)$ , arise from the loss of absorbing species in  $R$  with respect to  $R_0$ , and peaks pointing down, to  $-(R/R_0)$ , to the gain of absorbing species.

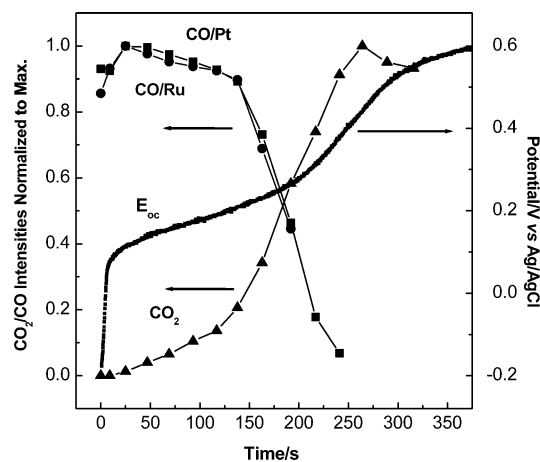
## Results and Discussion

Watanabe and Motoo<sup>3</sup> postulated that the cathodic process balancing the oxidation of adsorbed  $\text{CO}$  at open circuit involves the reduction of oxygen, and their data clearly showed very rapid OCP changes in oxygen saturated electrolyte. Our work also showed rapid OCP changes in oxygenated solution and oxidation of the adsorbed  $\text{CO}$  was complete before IR spectral data collection could be initiated. To slow this reaction, it was decided to purge the solution with  $\text{N}_2$  gas and thereby to reduce the oxygen concentration by about 2 orders of magnitude; this purge also served to remove the  $\text{CO}$  from solution prior to data collection. In each of the experiments reported below,  $\text{CO}$  was adsorbed at  $-200 \text{ mV}$  vs  $\text{Ag}/\text{AgCl}$  for 5 min, after which the electrolyte was sparged with nitrogen for 15 min prior to measurements being taken.

Figure 1 shows the spectrum collected at  $-200 \text{ mV}$  from the  $\text{Ru}_{\text{ads}}/\text{pc-Pt}$  electrode immediately after the adsorption of the  $\text{CO}$  at the electrode surface and the subsequent removal of the latter from solution, as well as the spectra taken subsequently at open circuit potential as a function of time. All the spectra in Figure 1 were normalized to the reference collected at  $+700 \text{ mV}$  at the end of the experiment where the surface was free from adsorbed  $\text{CO}$ .<sup>17,18</sup> Two clear gain features may be observed in Figure 1 near  $2070$  and  $2020 \text{ cm}^{-1}$ , both of which decrease in intensity with time at open circuit, and whose frequencies also show a shift; these bands may be attributed unambiguously on the basis of earlier data to  $\text{CO}$  species linearly adsorbed at on-top sites ( $\text{CO}_{\text{L}}$ ) at  $\text{Pt}$  and  $\text{Ru}$ , respectively.<sup>16–18</sup> This is a remarkable result as it is the first time to our knowledge that this partition has been clearly observed at smooth polycrystalline  $\text{Pt}$  electrodes. Moreover, it is in direct contrast to the emersion data of Hayden and colleagues but does suggest one explanation



**Figure 1.** In situ FTIR spectra collected during an experiment in which  $\text{CO}$  was adsorbed at  $-200 \text{ mV}$  vs  $\text{Ag}/\text{AgCl}$  from  $\text{CO}$  saturated  $0.1 \text{ M HClO}_4$  for 5 min. The solution was then sparged with  $\text{N}_2$ , and the first spectrum (I) collected. The circuit was then broken by disconnecting the working electrode and further spectra were taken as a function of time: (II) 1–16 s; (III) 17–32 s; (IV) 61–76 s; (V) 131–147 s; (VI) 181–196 s; (VII) 209–224 s; (VIII) 233–148 s. Some spectra have been omitted for clarity. The reference spectrum was taken at  $700 \text{ mV}$  at the end of experiment where the  $\text{Pt}/\text{Ru}$  surface was free from  $\text{CO}_{\text{ads}}$ .



**Figure 2.** Plots of the band intensities of the  $\text{CO}_{\text{L}}$  adsorbed at the  $\text{Pt}$  (■) and  $\text{Ru}$  (●) sites taken from the spectra in Figure 1. The intensity of the  $\text{CO}_2$  feature observed in the same experiment (in this case, the spectra in Figure 1 were normalized to the first spectrum, collected at  $-200 \text{ mV}$  where no  $\text{CO}_2$  was produced) and the open circuit potential ( $E_{\text{oc}}$ ) are also shown. The data at 0 s are those obtained from the spectrum collected at  $-200 \text{ mV}$  before the circuit was broken; see text for details.

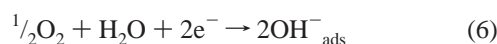
for the discrepancy; during any emersion process, our data clearly show that the  $\text{CO}_{\text{L,Ru}}$  species will be rapidly removed by their chemical reaction with adsorbed  $\text{OH}$  species/oxygen in solution (present at *ca.*  $10^{-5} \text{ M}$ ). In agreement with earlier work, no multiply bonded  $\text{CO}_{\text{ads}}$  species were observed on the polycrystalline  $\text{Pt}$  or  $\text{Ru}$  surfaces under the conditions of our experiment.<sup>18</sup>

On switching to open circuit, the open circuit potential (OCP) of the electrode began to alter swiftly (see Figure 2), rising to *ca.*  $+100 \text{ mV}$  over a few seconds, then more slowly to *ca.*  $+270 \text{ mV}$  over 200 s, and then accelerating up to *ca.*  $570 \text{ mV}$  after

350 s, whereafter it gradually tends toward an equilibrium value of ca. +700 mV (not shown for clarity). We observed similar behavior using a Ru(0001) electrode precovered with adsorbed CO in HClO<sub>4</sub>,<sup>19</sup> although the OCP in this system showed a steady rise to an equilibrium value of ca. +550 mV vs Ag/AgCl. Watanabe and Motoo<sup>3</sup> also observed a rise in the OCP to an equilibrium value on switching both polycrystalline (pc) Pt and Ru electrodes to open circuit; as in our experiments, their electrodes were immersed in aqueous H<sub>2</sub>SO<sub>4</sub> and precovered with adsorbed CO at a potential in the hydrogen adsorption region. They attributed the processes driving the change in OCP at the pc-Ru to reaction 3 or 4 (with M = Ru); in effect, we can write the anodic process contributing to the reactions represented by equations 3 and 4 as



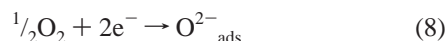
with the balancing cathodic reaction as



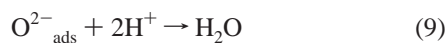
and



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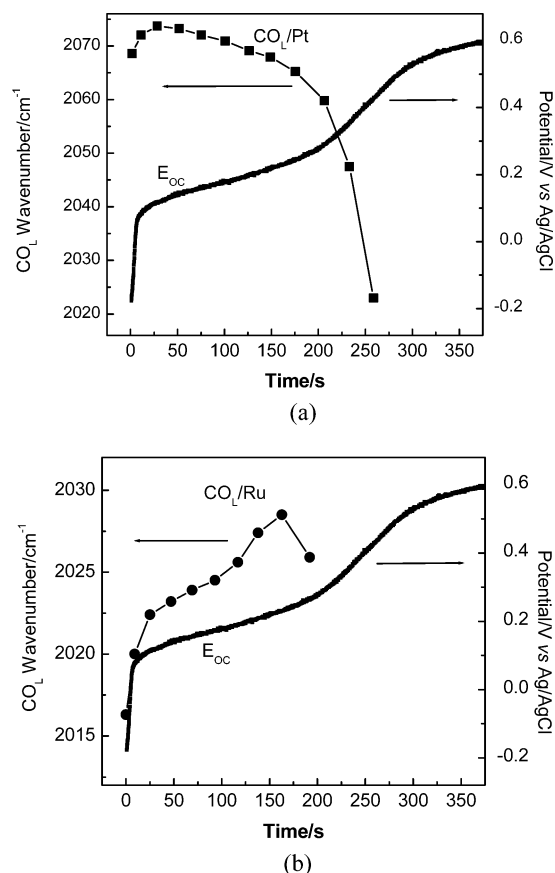


and



The initial rapid rise in OCP in Figure 2 is not observed in the absence of adsorbed CO, and correlates with an increase in the intensity of the CO<sub>L</sub> adsorbed at the Ru and Pt sites (CO<sub>L,Ru</sub> and CO<sub>L,Pt</sub>, respectively). The main potential-determining species present will be hydrogen, chemisorbed at the initial potential of -200 mV, and oxygen in solution. CO<sub>ads</sub> is not a potential-determining species, but its behavior is sensitive to potential, and removal of CO<sub>ads</sub> will require solution oxygen. Also, the much slower change in OCP in the absence of CO<sub>ads</sub> can be understood as a consequence of the much larger amount of H<sub>ads</sub>. Hydrogen is coadsorbed at -200 mV, either in the form of H atoms or as -CHO-type<sup>20</sup> species, and it may be the oxidation of the latter species that is responsible for the initial rapid increase in the CO<sub>L</sub> intensity (-CHO absorbs near 1750 cm<sup>-1</sup> and a feature in this region was not observed, but the absorption has a relatively low absorption coefficient<sup>20</sup>). However, it is clear that traces of oxygen (10 μM) are sufficient to remove this potential-determining species extremely quickly, suggesting that adsorbed hydrogen in whatever form can only be present in minute amounts. Therefore, the change in intensity of the CO<sub>L</sub> bands seen in the first few seconds cannot be due directly to oxidation of -CHO but must be due to reorientation of the off-normal CO<sub>L</sub> species<sup>18</sup> as the potential shifts by 300 mV.

The CO<sub>L,Ru</sub> and CO<sub>L,Pt</sub> features in Figure 1 both show a slow decrease up to 130 s after the initial increase in intensity in the first ca. 25 s, followed by a much more rapid drop at longer times; see Figure 2. It appears from Figure 2 that the rate of loss of CO<sub>L</sub> is the same for both the Ru and Pt sites and correlates quite well with the rate of gain of CO<sub>2</sub> (the oxidation product in the solution between the electrode and IR window);<sup>11–15</sup> if our assignment of the bands in Figure 1 is correct, then this



**Figure 3.** Plots of the C–O frequencies of the CO<sub>L</sub> adsorbed at the Pt (a) and Ru (b) sites in Figure 1 as a function of time. The data at 0 s are those obtained from the spectrum collected at -200 mV before the circuit was broken. The open circuit potential (*E*<sub>oc</sub>) is also shown.

is a remarkable result, as it strongly suggests a relatively free interchange of adsorbed CO<sub>L</sub> between Pt and Ru sites on the time scale of our experiment, which has not been postulated to date.

Figure 3a,b show the dependence of the CO<sub>L,Pt</sub> and CO<sub>L,Ru</sub> frequencies with time and also show the OCP data. Although the frequencies of both the CO<sub>L</sub> species on Pt and Ru domains showed the same sudden change/increase over the first ca. 25 s, as seen in Figure 2, and the same three-part behavior, they otherwise differ markedly in their otherwise with time, as expected from their assignment to the different metals. Thus, the CO<sub>L,Ru</sub> frequency rises steadily during the experiment, only falling at *t* > 160 s whereas the CO<sub>L,Pt</sub> frequency falls slowly after the initial sudden rise, followed by a more rapid decline at *t* > 160 s. Moreover, the rapid decrease in the CO<sub>L,Ru</sub> commences at OCP > 200 mV, the potential at which the active (1×1)-O(H) adlayer forms on Ru(0001).<sup>12</sup>

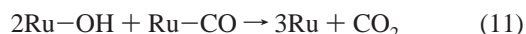
Interestingly, though the intensity data in Figure 2 (apart from the initial sudden rise) do not correlate very well with the OCP data, i.e., the rapid increase in CO<sub>2</sub> and decreases in CO<sub>L,Ru</sub> and CO<sub>L,Pt</sub> commence significantly before the rapid rise in the OCP at times greater than 150–175 s, the frequency changes do correlate quite well with the OCP data, showing the decrease in ν<sub>CO<sub>L,Ru</sub></sub> and a large decrease in ν<sub>CO<sub>L,Pt</sub></sub> at *t* > 150–175 s. This suggests that, once above some threshold value, the OCP initiates a relatively slow chemical oxidation process that is then largely not directly dependent upon the OCP, followed by the initiation of a second, faster process at longer times and higher OCP. We attribute the slower process, taking place up to ca. 115 s, to the oxidation of CO<sub>L</sub> at Pt\* sites, through diffusion



from Pt and the edges of the CO<sub>L</sub> islands on the Ru domains, according to



In effect, the CO<sub>L</sub> species adsorbed at the Pt and Ru sites are in equilibrium, with the leakage of the adsorbed CO species from the Ru domains to the Pt\* sites (where they are oxidized) freeing up the former and allowing for the formation of the electrocatalytically inert (2×2)-O(H)<sup>19</sup> adlayer (formed at potentials less than 200 mV on Ru(0001)). At longer times the onset of the faster process coincides with the onset potential for the formation of the active (1×1)-O(H)<sup>19</sup> adlayer on Ru(0001), and we tentatively suggest that the loss of the CO<sub>L,Ru</sub> species in this region is due to their reaction with this active hydroxide/oxide on the Ru surface according to



with free interchange still between Ru and Pt domains.

Considering the frequency data in Figure 3a,b in more detail, the  $\nu_{\text{CO}_{\text{L,Ru}}}$  data show a steady increase in frequency up to ca. 110 s, the OCP corresponding to onset of the formation of (1×1)-O(H), after which there is a rapid rise in frequency that correlates with a sharper increase in OCP until, at ca. 160 s, there is the onset of a much more rapid rise in OCP and a concomitant fall in the frequency of the CO<sub>L,Ru</sub> band. Given the fact that this time scale covers both the slow decrease in the intensity of the CO<sub>L,Ru</sub> band and its subsequent rapid decrease, this suggests<sup>11,17,18</sup> that the local CO<sub>ads</sub> coverage on Ru remains high, and so there is a steady increase in frequency as the OCP increases due to the Stark shift.<sup>11–15,20</sup> It is most likely that oxygen initially attacks the edges of the Ru islands on the Pt–Ru surface, and then migrates to form ordered islands such as (2×2)-O(H),<sup>11,19</sup> compressing the CO<sub>L,Ru</sub>, but not leading to immediate oxidation. Taken in conjunction with our earlier data on Ru(0001),<sup>11,12</sup> this suggests that the CO<sub>L,Ru</sub> species are oxidized at sites remote from the Ru at shorter times (i.e. potentials less than 200 mV), and the data are consistent with the model proposed here in which the CO<sub>L,Ru</sub> species diffuse from the periphery of the [CO + (2×2)-O(H)] islands to the Pt\* sites. At potentials greater than 200 mV, reaction takes place on the Ru islands, with the increasing (1×1)-O(H) hydroxide/oxide compressing the ever-shrinking [CO + (2×2)-O(H)] domains.<sup>11,12</sup> Only when the CO<sub>ads</sub> stripping from the Ru islands is well-advanced is the effect of the coverage dependence of the frequency of the CO<sub>L,Ru</sub> species observed as the fall in  $\nu_{\text{CO}_{\text{L,Ru}}}$ .

The behavior of the CO<sub>L,Pt</sub> frequency is in complete contrast to that observed for the CO<sub>L,Ru</sub> species, as expected from their attribution to CO<sub>L</sub> species in wholly different environments. After the initial sharp rise, the frequency of the CO<sub>L,Pt</sub> band decreases slowly up to ca. 115–138 s, at which point the onset of the (1×1)-O(H) layer on the Ru clearly impinges upon the behavior of the CO<sub>L</sub> species adsorbed at the Pt sites, as the CO<sub>L,Pt</sub> frequency shows a sharp decline. The initial slow decrease in  $\nu_{\text{CO}_{\text{L,Pt}}}$  may be attributed to the slow loosening of the CO<sub>L,Pt</sub> structure due to limited availability of the Pt\* sites and competition for these sites from CO<sub>L</sub> species diffusing from Ru sites. In contrast to the oxidation of the CO<sub>L,Ru</sub> species, oxidation of the CO adsorbed on Pt can be initiated by random diffusion, and so the local coverage does not remain high, and the decrease in coverage dominates the behavior of the CO<sub>L,Pt</sub>

frequency. At  $t > 138$  s, there is a rapid decrease in the intensity of the CO<sub>L,Pt</sub> band, and a more measured decrease in the frequency of this feature, which shows a more rapid decrease at  $t > 192$  s. In both the CO<sub>L,Pt</sub> and CO<sub>L,Ru</sub> cases, the rapid decrease in coverage leads the corresponding rapid change in frequency.

## Conclusions

Under open circuit conditions, our data strongly suggest that adsorbed CO on both the Ru and Pt domains is oxidized by the oxygen-containing adlayer on the Ru in a chemical process to produce CO<sub>2</sub> and that there is a free exchange of CO<sub>ads</sub> between the Ru and Pt sites. In essence, our model is that the initial potential determining species is a small amount of adsorbed hydrogen that can be quite rapidly oxidized even by the relatively small amount of oxygen left in the electrolyte. Once the hydrogen is stripped, oxygen is chemisorbed at the Ru edges of the Ru islands adjacent to the Pt\* sites and possibly also at the Pt\* sites. These adsorbed oxygens drive up the potential, causing the formation of the relatively inactive (2×2)-O(H) layer at potentials up to 200 mV (this takes time and the slow changes in CO<sub>ads</sub> on Ru and Pt that we observed below 200 mV reflect this), and then the more active (1×1)-O(H) layer at potentials above 200 mV where the more rapid changes in CO<sub>ads</sub> on the Ru and Pt sites take place. Over longer time scales, all the CO<sub>ads</sub> is oxidized, the Ru sites are fully covered by the (1×1)-O(H) layer and the potential rises to its equilibrium value.

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