

# Electrooxidation of adsorbed CO on Pt(1 1 1) and Pt(1 1 1)/Ru in alkaline media and comparison with results from acidic media

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## Abstract

Oxidation of adsorbed CO on Pt(1 1 1) and Pt(1 1 1)/Ru electrodes was studied in 0.1 M NaOH by the use of cyclic voltammetry and chronoamperometry. The data obtained in alkali are compared to those in 0.1 M H<sub>2</sub>SO<sub>4</sub>, and additional relevant information obtained with Pt(1 1 0) and Pt(1 0 0) surfaces is presented. We demonstrate, for the first time, that the voltammetric oxidation of CO on Pt(1 1 1)/Ru in alkali shows two clearly resolved CO stripping peaks, reminiscent of similar behavior in acids. On pure Pt(1 1 1), we confirm previous work that the voltammetric oxidation of a saturated CO adlayer in 0.1 M H<sub>2</sub>SO<sub>4</sub> and in 0.1 M NaOH yields a single and a split peak, respectively. Notably, we have found that while the CO oxidation on the Pt(1 1 1) electrode in acid occurs via a Langmuir–Hinshelwood mechanism, the CO oxidation in alkali in the pre-peak region is controlled predominantly via an Eley–Rideal (E–R) mechanism. On Pt(1 1 1)/Ru, the low potential CO oxidation in alkali occurs simultaneously through the L–H mechanism and the E–R mechanism. The addition of Ru to clean Pt(1 1 1) further improves the CO tolerance by promoting the oxidation of a greater fraction of the CO adlayer at low potentials. Therefore, the use of Pt/Ru catalysts in acidic and alkaline media may substantially reduce the CO poisoning that has so far limited low temperature fuel cell electrocatalyst performance, thus contributing to the development of more efficient direct oxidation fuel cells.

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## 1. Introduction

Electrooxidation of CO adsorbed on Pt and Pt/Ru surfaces is of interest to the theory and practice of direct oxidation fuel cells, since CO is produced as a poisoning species during the oxidation of small organic molecules on platinum-based catalysts [1]. Low-temperature direct oxidation fuel cells that employ an alkaline electrolyte possess clear kinetic advantages over acidic fuel cells. The improved anode performance [2], for instance, has been attributed to higher surface OH coverage, resulting in the oxidation of adsorbed CO at lower potentials. Cathode kinetics are also improved in alkaline media [3].

Although most work to date has been conducted in acidic media, several studies of CO oxidation on Pt in alkali have been published [2,4–12]. In addition, studies of methanol oxidation on Pt in alkaline media are to be noted [13–17], including some using Pt single crystals [18,19], and these studies have demonstrated a higher activity for methanol oxidation than in acid media. Tripković et al. propose that in alkaline media, methanol oxidation on Pt occurs primarily through a parallel mechanism (a dual path [20]) that does not involve formation of CO [21]. However, the formation of adsorbed CO in alkali has been detected by FTIR [15,16,19,22], resulting in a significant decrease in catalyst activity over time as the CO coverage increases. Therefore, as in acidic media [23], the activity of the catalyst may be improved by addition of a second metal, such as Ru, that can promote the oxidation of adsorbed CO. As is well known, the addition of Ru to Pt catalysts improves CO

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tolerance in acidic media, mostly by activating water at a lower potential than on pure Pt, but also through an electronic (ligand) effect [24]. A recent study showed that a supported Pt/Ru catalyst had significantly higher activity for methanol oxidation in alkaline media than a supported Pt catalyst at potentials below 0.6 V (vs. RHE) [25], confirming previous work [26,27].

The polymer electrolyte membrane fuel cell (PEMFC) typically uses an acidic, proton exchange polymer membrane as the electrolyte. So far, there has been little success in developing alkaline polymer membranes suitable for fuel cells despite some recent promising reports in this regard [28–32]. Likewise, problems caused by carbonation of the electrolyte have prevented commercialization of these overall quite efficient alkaline fuel cells, but electrolyte re-circulation and continuous CO<sub>2</sub> removal may prevent significant carbonation [3]. Notably, we are interested in the development of a membrane-free laminar flow fuel cell (LFFC), which shows promise as an alternative to the acid media PEMFC for some specific applications [33–35]. The LFFC is ideally suited to function as an alkaline fuel cell.

## 2. Experimental

The potentiostat used in these experiments was a Princeton Applied Research model 263A. A commercial Ag|AgCl ([Cl<sup>-</sup>] = 3M) electrode (BAS) was used as the reference electrode, but all potentials in this paper are quoted vs. the reversible hydrogen electrode (RHE). Hydrogen, argon (ultra high purity) and CO (Matheson purity) were purchased from Matheson. Other chemicals used were: NaOH and RuCl<sub>3</sub>·xH<sub>2</sub>O (Aldrich), HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> (GFS), and Millipore water.

The working single crystal electrode was a Pt bead, approximately 2 mm in diameter, cut and polished to expose the (1 1 1) surface. Also used were Pt(1 1 0) (3 mm diameter) and Pt(1 0 0) (6 mm diameter) crystals, as reference to the Pt(1 1 1) study. Prior to each experiment, the electrode was prepared by annealing in a H<sub>2</sub> flame, followed by cooling in an Ar + H<sub>2</sub> stream [36]. The electrode was protected by a drop of Millipore water during transfer to the electrochemical cell. Ru deposition was performed by spontaneous deposition from a 1 mM RuCl<sub>3</sub> in 0.1 M HClO<sub>4</sub> solution [37]. The deposition was carried out for 2 min, yielding Ru coverages of approximately 0.18, 0.09 and 0.21 ML for Pt(1 1 1), Pt(1 1 0), and Pt(1 0 0), respectively [38–43]. After deposition, the resulting oxides of Ru were reduced in 0.1 M NaOH by cycling the potential between 0.06 and 0.85 V at a sweep rate of 50 mV/s for six cycles.

Adsorption of CO was performed by immersing the electrode and bubbling CO through the solution for 5 min at a potential of 0.20 V (unless noted otherwise).

After adsorption, CO was purged from solution by Ar bubbling.

## 3. Results and discussion

### 3.1. CO oxidation on a pure Pt(1 1 1) electrode in 0.1 M NaOH

The background cyclic voltammogram (CV) of Pt(1 1 1) in 0.1 M NaOH (Fig. 1) is such as previously reported [21,44–47]. While the voltammetric features in the hydrogen adsorption region (0.0–0.40 V) are similar to those in acid, the interpretation of the region between 0.60 and 0.85 V, which shows a reversible peak, has been controversial. Although this peak has been assigned to adsorption of a strongly bonded hydrogen species, or to simultaneous adsorption of hydrogen and an oxygen-containing species [46,47], most evidence points to OH<sup>-</sup> adsorption as the peak origin [21,44,45]. At potentials higher than 0.90 V, an electric current corresponding to irreversible oxidation of the Pt surface is observed. Depending on the surface preparation technique, a small, reversible peak may also be observed at 0.48 V. This peak, absent from most published CVs of Pt(1 1 1) in alkaline media, was recently confirmed, but only on surfaces known to be clean and well-ordered [48]. In the present study, this peak was found after voltammetric cycling in the irreversible platinum oxide formation region or the hydrogen evolution region. For instance, eight scans between 0.06 and 1.25 V were found to produce a surface with a background voltammogram similar to the one shown in Fig. 1. The peak at 0.48 V may also be produced by scanning to higher potentials, but potentials higher than 1.25 V lead to the formation of surface defects. The concurrent presence of the peak at 0.48 V with significant defect features demonstrates

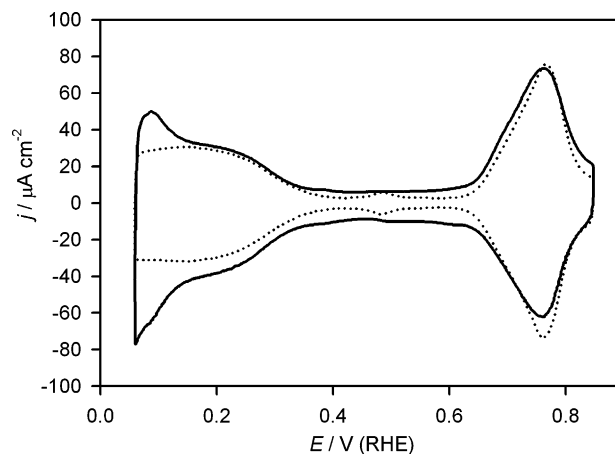


Fig. 1. Cyclic voltammograms of Pt(1 1 1) and Pt(1 1 1)/Ru in 0.1 M NaOH solution, (—) = Pt(1 1 1)/Ru, (···) = Pt(1 1 1). Scan rate = 50 mV/s.

that a high degree of surface ordering is not a prerequisite for observation of this peak. Since the 0.48 V peak was observed to grow under conditions known to create defects (i.e. scanning to high or low potential) it may be associated with a defect site. However, under carefully controlled conditions, this peak may become quite large while the features normally associated with defects are completely absent (as in Fig. 1).

After CO adsorption on the clean Pt(1 1 1) surface at 0.20 V, adsorbed CO was voltammetrically stripped at 50 mV/s. A background CV was collected immediately following CO stripping. Differences in quality and cleanliness of the Pt(1 1 1) crystal, as determined from the background CV, were found to produce different CO stripping voltammograms. Fig. 2(B) represents a typical CO stripping CV for a surface that did not show the reversible peak at 0.48 V. Three features are visible in the stripping voltammogram: a pre-wave at 0.5 V, a small peak at 0.65 V, and the main CO stripping peak at 0.79 V. A surface with a well-defined peak at 0.48 V yielded the stripping voltammogram shown in Fig. 2(C). This voltammogram shows a new peak (labeled peak I) at 0.55 V. The charge passed in this peak is approximately equal to the total charge in the pre-peak region for the previously mentioned electrode. Analysis of the CO stripping charge yields a total CO coverage for the Pt(1 1 1) electrode of  $0.66 \pm 0.02$  ML, which is very similar to the coverage obtained under the same conditions in 0.1 M H<sub>2</sub>SO<sub>4</sub> (also  $0.66 \pm 0.02$  ML). Higher CO coverages may be obtained by using shorter Ar purge times.

In acid, it is generally accepted [49–53] that oxidation of CO adsorbed on Pt(1 1 1) occurs mostly or entirely via a Langmuir–Hinshelwood (L–H) mechanism in which adsorbed CO reacts with an adsorbed oxygen-containing species, usually considered to be OH [2,50] or an activated surface water [54] (H<sub>2</sub>O<sub>ads</sub>):



Oxidation of adsorbed CO on Pt(1 1 1) in acid media has previously been studied using chronoamperometric experiments in which the potential of a CO-covered electrode in CO-free solution is stepped from the adsorption potential to a potential at which CO oxidation occurs. For an electrode that is initially CO-saturated, competition between CO<sub>ads</sub> and H<sub>2</sub>O<sub>ads</sub> (or OH<sub>ads</sub>) for surface sites results in a low initial current (corresponding to nucleation of oxygen-containing species) and a peaked current–time transient [49,51,52,55].

The results of a similar potential-step experiment in alkaline media (Fig. 3) demonstrate a fundamental mechanistic difference between acid and alkaline media for oxidation of adsorbed CO on Pt(1 1 1). A step from the adsorption potential (0.20 V) to a potential in the vicinity of the first CO stripping peak (the peak I region) results in the monotonically decaying current–time

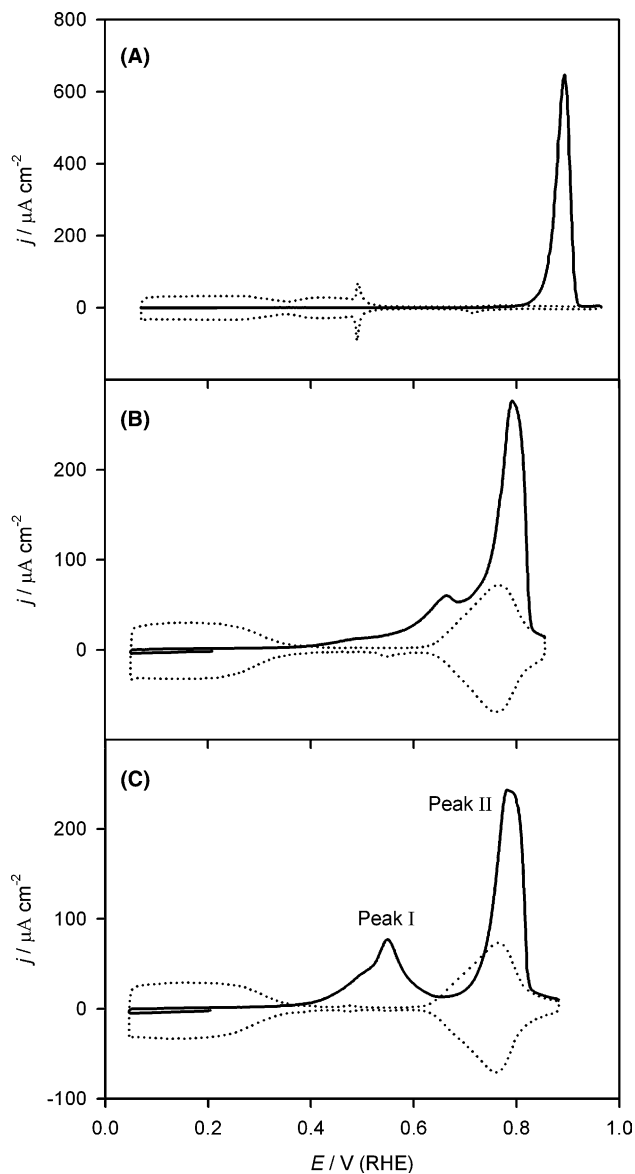
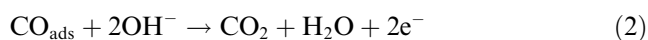


Fig. 2. Voltammetric oxidation of adsorbed CO on Pt(1 1 1) in CO-free solution, (—) = CO stripping, (···) = background. (A) 0.1 M H<sub>2</sub>SO<sub>4</sub> solution; (B) and (C) 0.1 M NaOH solution. In C, the potential was scanned up to 1.25 V eight times prior to CO adsorption; in B the potential was always maintained below 0.9 V. Scan rate = 50 mV/s, background CV collected immediately after CO stripping.

transient shown in the first part of Fig. 3, in which a significant fraction of the adsorbed CO is oxidized. Two alternate mechanisms may be proposed to explain this behavior: an Eley–Rideal (E–R) mechanism or a L–H mechanism involving non-competitive adsorption of CO and OH or H<sub>2</sub>O. The E–R mechanism involves attack by solution-phase OH<sup>−</sup> on the adsorbed CO:



An E–R reaction involving H<sub>2</sub>O is also possible, but attack by solution-phase OH<sup>−</sup> is a more probable explanation of the difference in the mechanism between

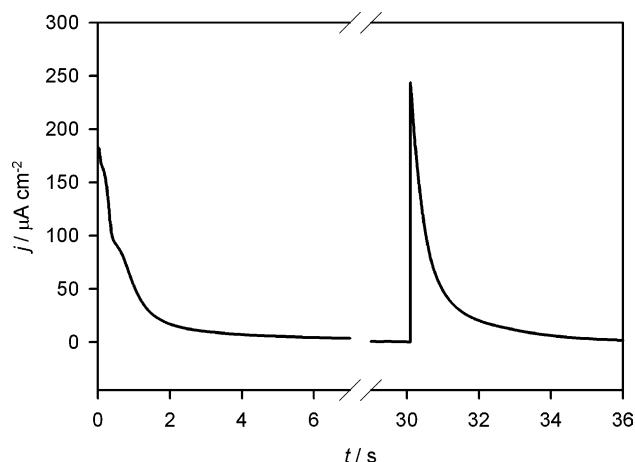


Fig. 3. Double potential step chronoamperometry of CO oxidation on Pt(111) in CO-free 0.1 M NaOH solution. The potential was stepped from  $E_{\text{ads}}$  (0.20 V) to 0.54 V for 30 s, followed by a step to 0.77 V.

alkaline and acidic media, since the concentration of  $\text{OH}^-$  is many orders of magnitude higher in alkali. An E–R mechanism involving  $\text{OH}^-$  was proposed by Sun and Chen to explain the oxidation of adsorbed CO on polycrystalline Pt in NaOH solution at potentials less positive than the OH adsorption region, as well as the decrease in the onset potential for CO oxidation resulting from an increase in pH [8]. In sulfuric acid media, Bergelin et al. proposed an E–R mechanism involving solution-phase  $\text{H}_2\text{O}$  to explain the current–time plateau, indicative of a reaction that is of order zero in OH (or  $\text{H}_2\text{O}_{\text{ads}}$ ), that occurs in the early stages of oxidation of a saturated CO adlayer on Pt(111) [53]. However, Lebedeva et al. have suggested that this plateau region can be explained by a L–H reaction in which the initially saturated CO adlayer relaxes to fill unoccupied sites in the early stages of CO oxidation, maintaining a constant coverage of OH (or  $\text{H}_2\text{O}_{\text{ads}}$ ) [49].

Notice that bulk CO oxidation in the double layer region and the hydrogen region on Pt(111) in alkali has been attributed to OH adsorbed on defect sites [2]. A theoretical study provided some evidence for this proposal, predicting that OH adsorption may be possible at potentials much lower than the typically observed onset potential of surface oxidation ( $\approx 0.60$  V) [56]. Similarly, the observed monotonically decaying CO oxidation current may be explained using a L–H mechanism involving non-competitive adsorption of oxygen-containing species at defects. However, studies of CO stripping on vicinal (111) surfaces in sulfuric acid have demonstrated that, although some oxygen-containing species appears to adsorb at (100) and (110) steps at low potential [57], CO and the oxygen-containing species still compete for adsorption sites, resulting in a peaked current–time transient [58]. This, as well as the fact that our Pt(111) surfaces are essentially defect free (Fig. 1), suggests that the observed monotonically decaying cur-

rent in the peak I (pre-peak) region is best described in terms of the E–R mechanism.

We also studied the oxidation of pre-adsorbed CO on Pt(110) and Pt(100) in 0.1 M NaOH solution by voltammetry and chronoamperometry. Here, the focus was on evaluating further the feasibility of an E–R mechanism in the pre-peak region. If the proposed E–R mechanism is operative, the CO oxidation rates would not be expected to display the strong surface structure dependence that is characteristic of L–H kinetics [59].

The data obtained are the following. As expected, the voltammetric CO oxidation morphology is different for the three surfaces, as shown in Fig. 4; well-known be-

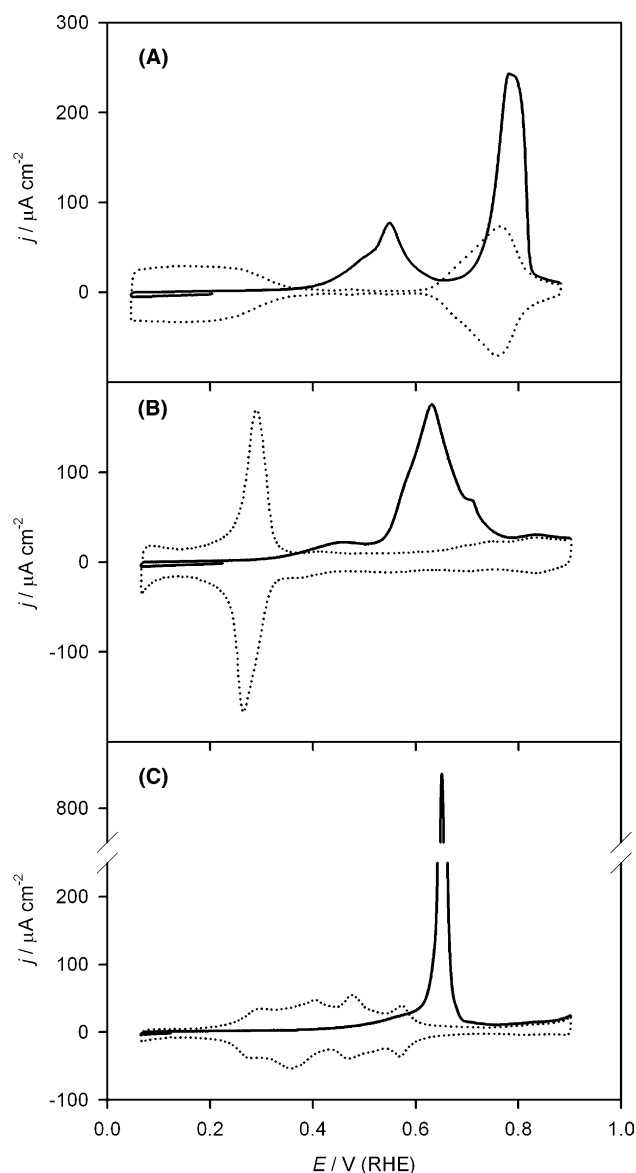


Fig. 4. Voltammetric oxidation of adsorbed CO on Pt(*hkl*) in CO-free 0.1 M NaOH solution, (—) = CO stripping, (---) = background. (A) Pt(111); (B) Pt(110); (C) Pt(100).  $E_{\text{ads}} = 0.20$  V for Pt(111) and Pt(110), 0.10 V for Pt(100). Scan rate = 50 mV/s, background CV collected immediately after CO stripping.

havior of single crystal electrodes. In each case, however, there is a pre-peak region and a main peak region. Potentiostatic CO oxidation at 0.53 V (in the pre-peak region for all three surfaces) results in an initially decaying current, with a peaked profile (corresponding to oxidation of the main voltammetric CO peak) developing at longer times for Pt(110) and Pt(100). This peaked behavior results in a non-zero baseline current during the early stages of the current transient. With an assumed constant value for this baseline, the current transient can be approximated as an exponential decay, as expected for the E–R oxidation of CO, which should be approximately first order in CO. The data for times prior to the onset of the peak (Fig. 5) were fitted using a first order rate law (Eq. (3)) to estimate the rate constant ( $k$ ) for CO oxidation in the pre-peak region.

$$j = j_0 \exp(-kt). \quad (3)$$

The estimated  $k$  values are 1.5, 2.3, and 1.8 s<sup>-1</sup>, and the  $R^2$  values of the fit are 0.986, 0.998, and 0.992 for Pt(111), Pt(110), and Pt(100), respectively. Clearly, the close agreement between the rate constants for the different surfaces is further evidence for an E–R mechanism, which is expected to be only mildly structure sensitive since OH (or H<sub>2</sub>O) does not have to adsorb in this reaction.

Whereas CO oxidation in the pre-peak region has been shown to occur most probably through the E–R mechanism, in the main peak region the reaction is L–H for all three surfaces studied. For the Pt(110) and Pt(100) surfaces, this is indicated by the peaked current transient following the initial E–R decay (not shown). For the Pt(111) surface, no peak is observed in the current transient following a step to 0.77 V (Fig. 3). However, this may be explained by the high fraction of CO oxidized in the pre-peak region (≈50%). Complete oxidation of CO in the pre-peak opens enough sites for OH adsorption that no peak is observed in the current transient following a potential step to the main peak region.

### 3.2. CO oxidation on Pt(111)/Ru electrode in 0.1 M NaOH

Spontaneous deposition of Ru on the Pt(111) surface results in the formation of nanoscale islands of Ru [41]. The resulting CV of the nanoscale decorated Pt(111) surface in 0.1 M NaOH solution (Fig. 1) is basically similar to the clean Pt(111) CV, but the double layer capacitance is larger, and a new reversible peak appears in the hydrogen adsorption region, which has previously been assigned to hydrogen adsorption on Ru [60]. The peak observed at 0.48 V on clean Pt(111) is not observed on Pt(111)/Ru.

On such Pt surfaces covered with Ru islands and exposed to CO chemisorption, a study using Monte

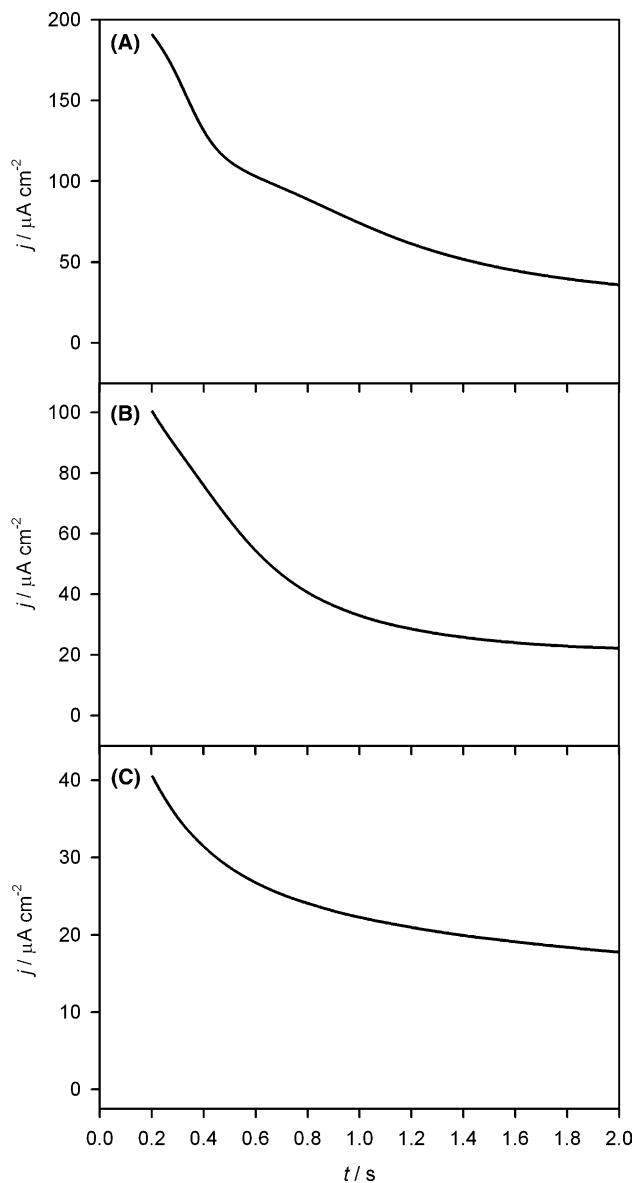


Fig. 5. Potentiostatic oxidation of preadsorbed CO on Pt( $hkl$ ) in CO-free 0.1 M NaOH solution following a step from  $E_{\text{ads}}$  (0.20 V for Pt(111) and Pt(110), 0.10 V for Pt(100)) to 0.53 V. (A) Pt(111); (B) Pt(110); (C) Pt(100).

Carlo simulations yielded a splitting of the main CO stripping peak into two peaks [61]. Both peaks were predicted to occur at lower potentials than the CO stripping peak on clean Pt. This peak splitting has been observed experimentally on Pt(111)/Ru in acid electrolytes [62–65]. A peak at lower potential has been interpreted as oxidation of CO adsorbed on and adjacent to Ru islands, hereafter denoted as Pt(111)/Ru–CO, and a peak at more positive potential corresponds to CO stripping from Pt(111) domains far from the Ru islands, denoted as (Ru)Pt(111)–CO [62]. The results of the present study demonstrate similar peak splitting in alkali. Stripping voltammograms of saturated CO

adlayers on Pt(1 1 1)/Ru electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub> [62] and 0.1 M NaOH (with equal Ru coverage) are compared in Fig. 6. In acid, the peak due to (Ru)Pt(1 1 1)–CO oxidation (peak II) occurs at 0.66 V, a negative shift of 0.23 V from the potential of the corresponding peak on clean Pt(1 1 1) (at the sweep rate of 50 mV/s). In alkali, the peak potentials are approximately the same for Pt(1 1 1)/Ru (0.58 and 0.74 V for peaks I and II, respectively) as they are for clean Pt(1 1 1) (0.55 and 0.79 V). However, a significant redistribution of charge between the two peak regions results in more CO being stripped at lower potential on Pt(1 1 1)/Ru than on clean Pt(1 1 1) in alkali.

Oxidation of preadsorbed CO on Pt(111)/Ru is compared with CO stripping on Pt(110)/Ru and Pt(100)/Ru in Fig. 7. The peak splitting is much weaker on these latter surfaces than on Pt(1 1 1)/Ru. Oxidation of preadsorbed CO on the Pt(1 1 0)/Ru surface shows a prewave at 0.51 V and a main peak at 0.58 V. The splitting is even weaker for the Pt(100)/Ru surface, which shows a shoulder at 0.60 V and a main peak at 0.63 V.

A comparison of Fig. 6(A) and (B) shows that the onset of CO stripping on Pt(1 1 1)/Ru occurs at lower

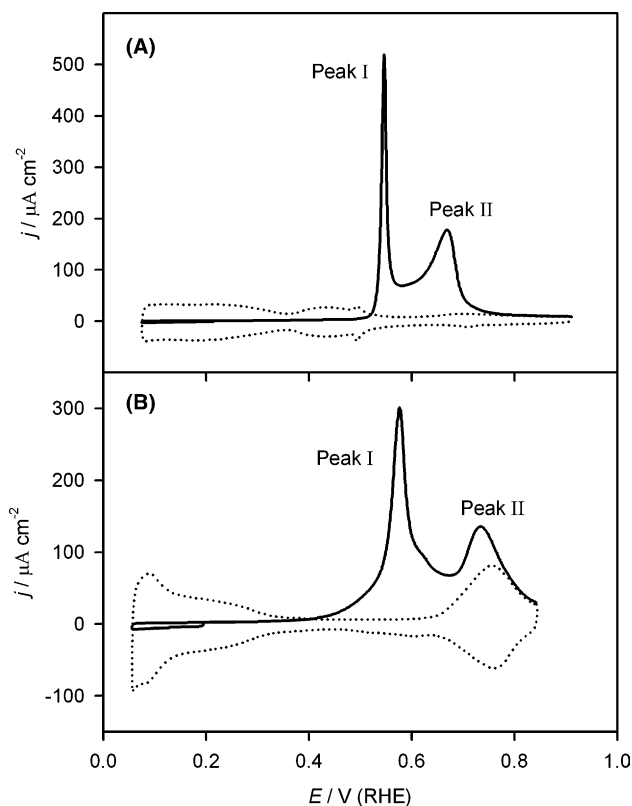


Fig. 6. Voltammetric CO oxidation on Pt(1 1 1)/Ru in CO-free solution, (—) = CO stripping, (···) = background. (A) 0.1 M H<sub>2</sub>SO<sub>4</sub> solution (20 min. Ar purge); (B) 0.1 M NaOH solution (5 min Ar purge). Scan rate = 50 mV/s, background CV collected immediately after CO stripping.

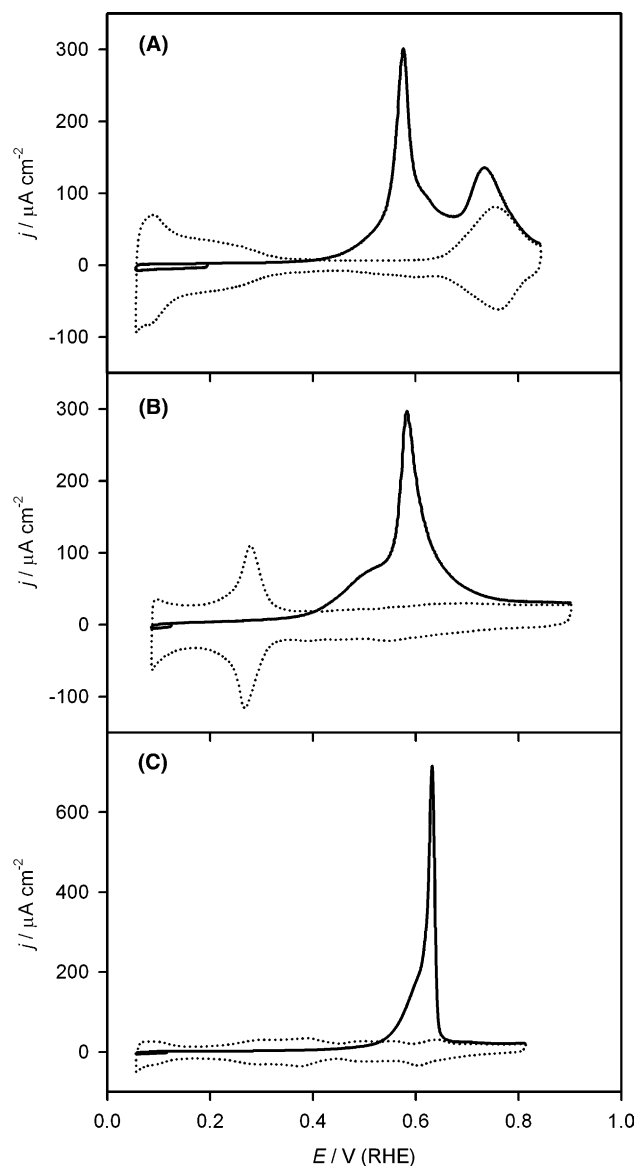


Fig. 7. Voltammetric oxidation of adsorbed CO on Pt(*hkl*)/Ru in CO-free 0.1 M NaOH solution, (—) = CO stripping, (···) = background. (A) Pt(1 1 1)/Ru; (B) Pt(1 1 0)/Ru; (C) Pt(1 0 0)/Ru.  $E_{\text{ads}} = 0.20$  V for Pt(1 1 1)/Ru, 0.10 V for Pt(1 1 0)/Ru and Pt(1 0 0)/Ru. Scan rate = 50 mV/s, background CV collected immediately after CO stripping.

potential in alkali than in acid. A significant CO stripping current appears at 0.40 V in alkali vs. 0.50 V in acid, although in both media, very small stripping currents occur even at potentials in the hydrogen region.

Analysis of the distribution of charge between the two CO stripping peaks reveals another difference between acid and alkali: in acid, approximately 33% of the stripping charge passes in the lower potential peak (peak I), attributed to Pt(1 1 1)/Ru–CO stripping, and 67% in peak II, attributed to (Ru)Pt(1 1 1)–CO stripping. In alkali,  $\approx 80\%$  of the charge is passed in peak I, and  $\approx 20\%$  in peak II. This difference suggests that, in alkali, peak I consists of both Pt(1 1 1)/Ru–CO oxidation and

oxidation of a significant fraction of the (Ru)Pt(1 1 1)–CO. Since a CO stripping peak is observed on clean Pt(1 1 1) in alkali at 0.55 V, it is reasonable to suppose that some CO would be stripped from the (Ru)Pt(1 1 1) domains even at low potential.

The CO adsorption potential ( $E_{\text{ads}}$ ) was found to influence the alkaline CO stripping voltammogram of the Pt(1 1 1)/Ru surface (Fig. 8). For potentials at which insignificant CO oxidation occurs (i.e.  $E_{\text{ads}} < 0.25$  V), the stripping voltammogram does not change with  $E_{\text{ads}}$ . For  $E_{\text{ads}} > 0.25$  V, the oxidation of a part of the adsorbed monolayer during Ar purging results in a lower CO coverage, and peak I is shifted to less positive potentials due to the increased availability of sites for OH adsorption (assuming a L–H mechanism for oxidation of Pt(1 1 1)/Ru–CO, see below). At  $E_{\text{ads}} = 0.30$  V, peak I is greatly decreased, and the presence of an additional peak at approximately 0.60 V becomes clearer. These results indicate that peak I represents more than one population of adsorbed CO.

After CO adsorption and Ar purging in 0.1 M NaOH, CO that strips in the peak I region may be oxidized with negligible effect on peak II (Fig. 9) by stepping the electrode potential to 0.56 V for 30–60 s, as reported below. That is, the CO oxidation in the two surface domains may be studied independently of one another. The results from double potential step chronoamperometry in 0.1 M NaOH are shown in Fig. 10. These results are similar, but not identical, to previous results obtained in sulfuric acid electrolyte [62]. In particular, it is noteworthy that the current in the first step has a large positive value at  $t \approx 0$  s (corrected for double layer charging). This is illustrated more clearly in Fig. 11, which shows the current transient recorded after a step to 0.46 V. For L–H CO oxidation on an initially

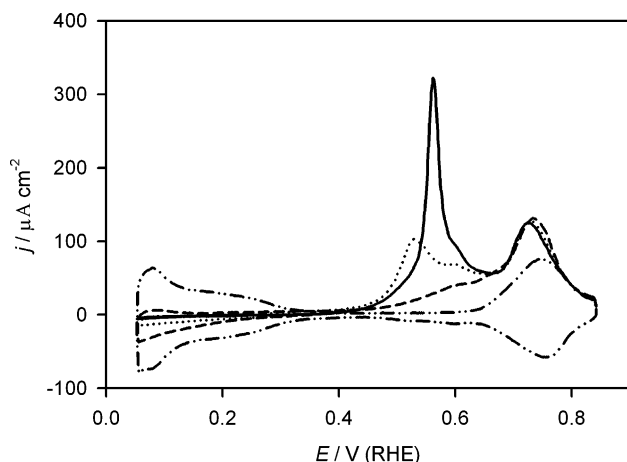


Fig. 8. Voltammogram CO oxidation on Pt(1 1 1)/Ru in CO-free 0.1 M NaOH solution: effect of potential of adsorption on CO stripping. Values of  $E_{\text{ads}}$ : (—) = 0.25 V, (···) = 0.30 V, (- - -) = 0.35 V. Background = (- · - ·). Scan rate = 50 mV/s.

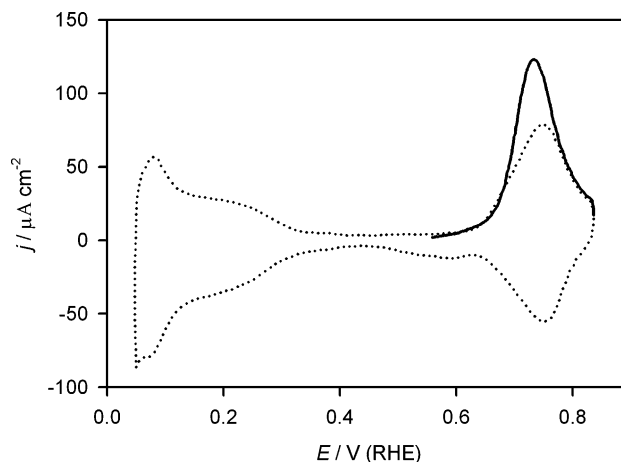


Fig. 9. Voltammogram CO oxidation on Pt(1 1 1)/Ru in CO-free 0.1 M NaOH solution after a potential step from  $E_{\text{ads}}$  (0.20 V) to 0.56 V for 60 s, (—) = CO stripping, (···) = background. Scan rate = 50 mV/s, background CV collected immediately after CO stripping.

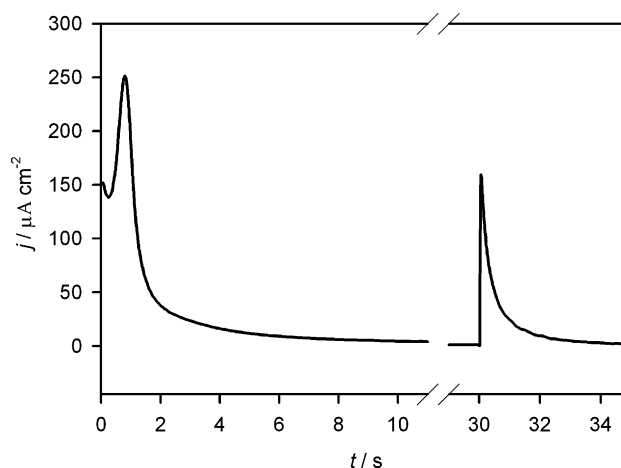


Fig. 10. Double potential step chronoamperometry of CO oxidation on Pt(1 1 1)/Ru in CO-free 0.1 M NaOH solution. Potential was stepped from  $E_{\text{ads}}$  (0.20 V) to 0.56 V for 30 s, followed by a step to 0.71 V.

CO-saturated electrode, the current would be expected to be approximately zero at  $t \approx 0$  s, as has been observed in acid [62]. Furthermore, the current shows a slight decay before the onset of the peak. Therefore, a more complicated mechanism is required to describe CO oxidation in the first potential step. Such a mechanism may, for instance, take the form of two overlapping processes: oxidation of CO from Pt(1 1 1)–Ru sites via a L–H mechanism (yielding a peaked current–time transient with  $j \approx 0 \mu\text{A}/\text{cm}^2$  at  $t \approx 0$  s), and the simultaneous oxidation of (Ru)Pt(1 1 1)–CO via the E–R mechanism (see above for the CO oxidation on pure Pt(1 1 1) surface).

The current–time transient resulting from the second potential step ( $E = 0.71$  V) in Fig. 10 shows an

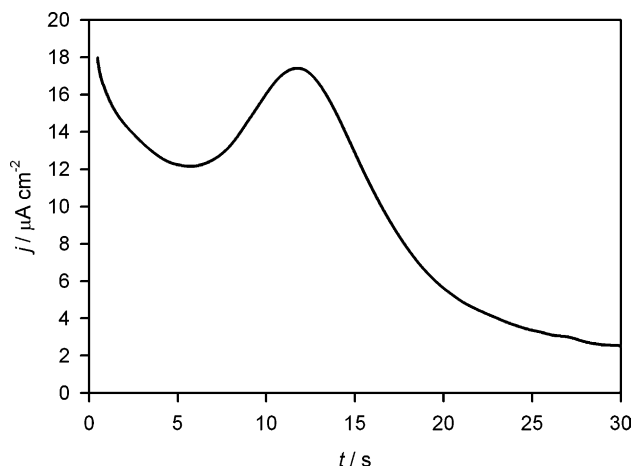


Fig. 11. Potentiostatic CO oxidation on Pt(1 1 1)/Ru in CO-free 0.1 M NaOH solution. Potential was stepped from  $E_{\text{ads}}$  (0.20 V) to 0.46 V.

approximately exponential decay. In acid, a similar observation was explained in terms of oxidation of CO adsorbed on Pt sites by OH adsorbed near the Pt/Ru edge. The same explanation may hold in alkali; however, since a significant fraction of the (Ru)Pt(1 1 1)–CO is oxidized in the first potential step, the number of sites available for adsorption of oxygen-containing species in the second potential step is high enough that the current–time transient would not show a peak even for competitive CO and OH adsorption. Therefore, further study is needed to determine the mechanism of CO oxidation at potentials in the peak II region.

In acid, the current–time decay during (Ru)Pt(1 1 1)–CO oxidation was shown to occur in two distinct time

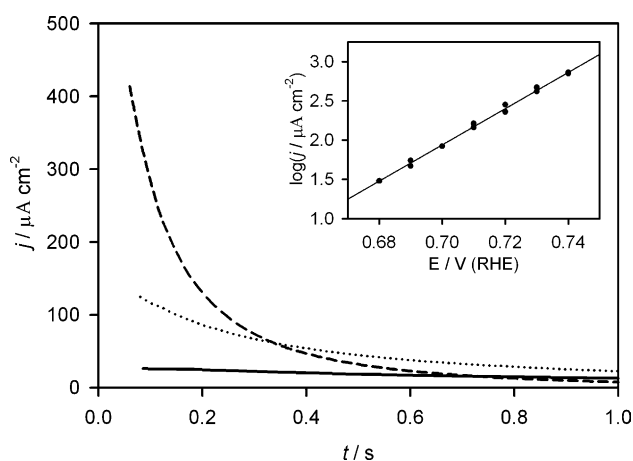


Fig. 12. Current-time transients for potentiostatic CO oxidation on Pt(1 1 1)/Ru in CO-free 0.1 M NaOH solution following a potential step from 0.56 V to a potential in the peak II region: (---) = 0.74 V, (···) = 0.71 V, (—) = 0.69 V. After CO adsorption and Ar purging, the potential was stepped from  $E_{\text{ads}}$  (0.20 V) to 0.56 V for 30 s to remove CO in the peak I region. Inset: the Tafel slope is approximately 40 mV/decade below 0.74 V.

regimes [62]. At short times ( $t < 50$  ms) the current decayed rapidly, with a Tafel slope of 120 mV/decade. This result was interpreted as evidence for the formation of reactant pairs between OH adsorbed at Pt sites adjacent to Ru islands and CO adsorbed on neighboring Pt sites. At longer times, current decay was more gradual, with a Tafel slope of 60 mV/decade. In alkali, the existence of two time domains could not be probed due to a large overlapping OH adsorption current, which obscures the CO oxidation current. At longer times, we found an approximate Tafel slope of  $\approx 40$  mV/decade for potentials below 0.74 V (Fig. 12).

#### 4. Conclusions

The results of this study demonstrate that oxidation of CO adsorbed on Pt(1 1 1) and Pt(1 1 1)/Ru in alkaline media cannot be modeled as a simple L–H reaction between competitively adsorbed CO and OH (or adsorbed water molecules) [49,51,52,55]. Instead, on pure Pt(1 1 1), the CO oxidation at potentials less positive than the onset of surface oxidation is best explained in terms of the E–R reaction between adsorbed CO and  $\text{H}_2\text{O}$  or (more likely)  $\text{OH}^-$  in the outer Helmholtz plane. On Pt(1 1 1)/Ru, the CO oxidation at low potentials may be explained in terms of the L–H reaction between the competitively adsorbed CO and OH (on Ru sites) superimposed upon the E–R mechanism (on Pt sites far from Ru).

Oxidation of pre-adsorbed CO on Pt(1 1 1)/Ru in 0.1 M NaOH is similar to CO stripping in 0.1 M  $\text{H}_2\text{SO}_4$ , as both media show a splitting of the CO stripping current into two peaks. However, while the peak at lower potential in acid is attributed to the oxidation of CO adsorbed on and strictly around the Ru islands, in alkali, this peak includes a high degree of CO oxidation on Pt sites more distant from the Ru islands. This difference causes the lower potential peak to contain a much higher fraction of the total CO stripping charge in alkali ( $\approx 80\%$ ) than in acid ( $\approx 33\%$ ). In both cases the peaks at higher potentials are due to CO oxidation on Pt sites far from the Ru islands.

The onset of CO stripping on Pt(1 1 1)/Ru occurs at lower potential in alkali than in acids (at  $\approx 0.25$  V). This result provides further evidence for a likely advantage of alkaline media for electrooxidation of methanol and, most probably, for other small organic molecules that produce CO as an intermediate and/or poisoning species during electrooxidation. Since the use of alkaline media also improves the kinetics of the oxygen reduction reaction [3], alkaline direct oxidation fuel cells may prove to be superior to acidic cells, particularly with the use of Pt/Ru anode electrocatalysts, as demonstrated by the present investigation.



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