# Enhancement in methanol oxidation by spontaneously deposited ruthenium on low-index platinum electrodes

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Received 12 August 1997; accepted 11 November 1997

Using Auger electron spectroscopy and electrochemistry we confirm that ruthenium is spontaneously deposited on platinum single-crystal faces from ruthenium(III) chloride solutions in perchloric acid. The deposit is catalytically active towards methanol present in electrolytic media. On the Pt(111) surface – the most active catalyst for the oxidation process – the data show that the packing density of ruthenium is 9.9 ± 1.5% and increases with ruthenium concentration in the electrolytic bath, confirming the previous electrochemical coverage estimate. In the most favorable instances the *ruthenium enhancement* factor, the current ratio due to methanol oxidation with and without ruthenium on the surface, is equal to15 (at 0.490 V vs. RHE reference on Pt(111)). We believe this study is an important addition to our long-range efforts in investigating surface structure effects in platinum–ruthenium heterogeneous electrocatalysis.

**Keywords:** well-ordered electrodes, platinum/ruthenium catalysts, methanol, Auger electron spectra

## 1. Introduction

Of interest to our group are surface structure effects in heterogeneous electrocatalysis including the application of well-defined, single-crystal electrodes [1–3] and catalytic nanoparticles investigated by solid-state NMR [4,5]. In the first category, the methanol oxidation process on ruthenium films on platinum single-crystal faces is investigated [6,7]. Such platinum-supported Ru-films can be perceived as versatile models of “real-world” electrocatalysts since, for instance, Pt/Ru deposits on graphite are used as an anode in the direct oxidation methanol fuel cell (ref. [8] and references therein). However, despite the general consensus that the Pt/Ru catalyst works for methanol oxidation on some level, there is very little insight into what is the magnitude of surface structure effects in the oxidation rates, and what are the mechanistic details of this catalytic reaction [9–12] in the atomic/molecular perspective. In order to generate state-of-the-art answers to the questions formulated above, we have already studied and reported on thin ruthenium films on the Pt(111), Pt(100) and Pt(110) surfaces [13], and provided evidence for the strong drive of ruthenium to become spontaneously deposited on these surfaces. We have also made estimates of the ruthenium coverages based upon voltammetric data [13]. Below, using the Pt(111) electrode, we confirm the spontaneous deposition of ruthenium by the use of Auger electron spectroscopy, quantify the amount of deposited ruthenium, and show that the deposit is electroactive towards methanol dissolved in acidic media. We will mainly focus on the Pt(111) electrode covered by ruthenium since, as we will document below (see also ref. [7]), the Pt(111)/Ru is the best catalyst for the methanol oxidation process. We believe this study is an important addition to our investigations of surface structure effects in platinum–ruthenium heterogeneous electrocatalysis [6,7].

## 2. Experimental

The spontaneous deposition of ruthenium was carried out from electrolytic bath solutions prepared by dissolving $5 \times 10^{-5}$ and $5 \times 10^{-4}$ M of $RuCl_3$ in 0.1 M $HClO_4$, as recently reported [13]. Millipore water (18 MΩ cm), Alfa Aesar ruthenium(III) chloride, $RuCl_3 \cdot xH_2O$ and GFS Chemicals ultra-pure grade perchloric acid were used for the solution preparation. In all electrochemical measurements, the Pt(111) working electrode was used in a meniscus configuration. The real surface area of this electrode was determined using hydrogen adsorption–desorption charges [13]. Prior to electrochemical studies, the solutions were deaerated and blanketed with argon (99.999%). All measurements were conducted at room temperature, 25 ± 1°C, and all potentials are presented vs. the reversible hydrogen electrode (RHE) reference.

The characterization part of this project was carried out by Auger electron spectroscopy (AES) using the UHV-electrochemistry instrument described elsewhere (ref. [14] and references therein). A Pt(111) single crystal, Aremco, 6 mm diameter, was used as the working electrode. The surface was cleaned by argon ion sputtering and was oxygen treated at 800°C to remove traces of impurities left after ion sputtering. The clean and ordered (verified by low-energy electron diffraction) sample was transferred, without exposure to air, to the system antechamber for electrochemical measurements

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using a conventional three-electrode circuitry, ultra-clean argon environment, and a fully computerized EG&G PAR 273 potentiostat.

For the experiments not involving the UHV methodology, a flame-annealed [15] Pt(111) electrode of 0.2 cm diameter was used. Oxidation of methanol (Fisher, ACS certified) and other electrochemical measurements were conducted under chronoamperometric conditions in a free standing, three-electrode cell equipped with a Luggin capillary. The cell solution was 0.10 M $HClO_4 + 0.60$ M $CH_3OH$. After ruthenium deposition, and before methanol oxidation, the Pt/Ru surface was "activated" by two cyclic voltammetric cycles in 0.10 M $HClO_4$ solution.

## 3. Results and discussion

### 3.1. Electrochemical estimate of the spontaneously deposited ruthenium

The cyclic voltammetric curve of the Pt(111) electrode (figure 1A) exposed to the ruthenium-containing solution (Experimental), measured in clean 0.1 M $HClO_4$ exhibits an increase in the reduction current in the double layer and hydrogen range (figure 1B). As reported previously, this can be attributed to the spontaneously deposited ruthenium present on the surface [13]. Due to the deposition, there is also a noticeable suppression of the anion adsorption/desorption charge in the so-called "butterfly" region characteristic of the reversible adsorption/desorption of perchlorate anions [16,17].

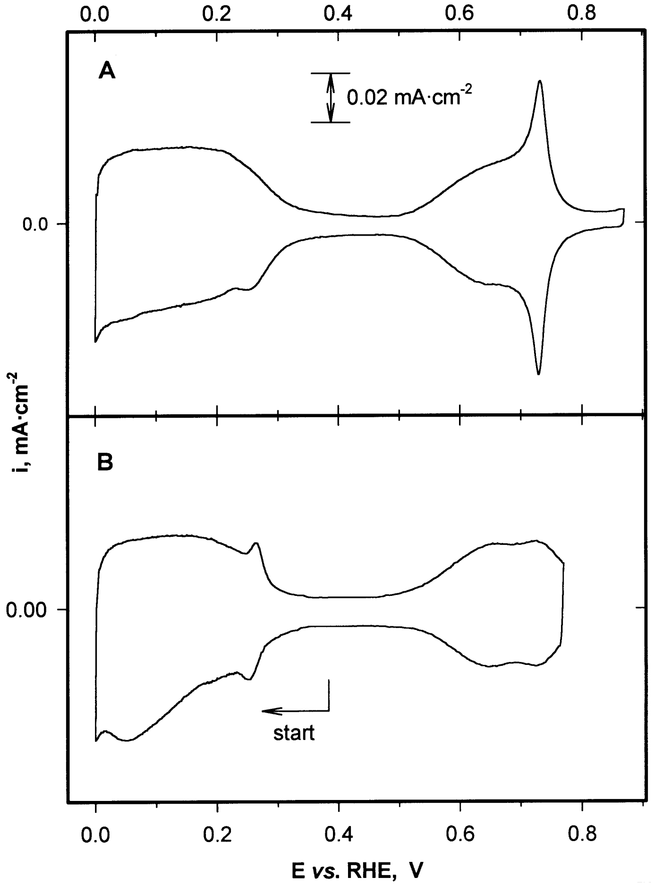

Figure 1. (A) Cyclic voltammogram of a clean Pt(111) electrode in 0.1 M $HClO_4$ solution at 50 mV $s^{-1}$. (B) First CV scan of the Pt(111) electrode after spontaneous deposition of ruthenium in $5 \times 10^{-5}$ M $RuCl_3 + 0.1$ M $HClO_4$ during 2 min. The scan began at "START" at 50 mV $s^{-1}$.

The coverage of the spontaneously deposited ruthenium, $\theta_0$, can be estimated by the use of electrochemical method [13] as demonstrated in figure 2. The procedure involves several steps, (i) a platinum electrode is exposed to the $RuCl_3$-in-0.1 M $HClO_4$ solution at open circuit (Experimental), (ii) the surface is covered by ruthenium using electrolysis in the same solution as in (i), (iii) the electrolysis charge involved in the reaction

$$RuO^{2+} + 2H^+ + 4e \rightarrow Pt{-}Ru^0 + H_2O \qquad (1)$$

is measured, and a coverage of ruthenium, $\theta(q)'$, as a function of the electrodeposition charge is obtained (assuming a 100% yield in the electrolysis), (iv) cyclic voltammetric curves for such electrodes are recorded in 0.10 M $HClO_4$, and a voltammetric feature, defined as $\Delta$, that was clearly responding to ruthenium addition, is identified. Finally, $\Delta$ is plotted as a function of ruthenium coverage. For the (111) face, $\Delta$ is the difference between the reduction current at a given ruthenium coverage and at the clean Pt(111) electrode at 0.4 V (approximately in the middle of the double-layer range). In figure 2, $\Delta$ is plotted vs. $\theta(q)'$ and figure 2 inset demonstrates how $\Delta$ was actually measured. A straight line of $\Delta$ vs. $\theta(q)'$ is found which does not pass through the origin, and yields $\theta(t)'$ at $\Delta = 0$ defined as $\theta_0'$, a negative value. $\theta_0$, equal to $-\theta_0'$ is the coverage of the spontaneously deposited ruthenium equal, for Pt(111), to $0.10 \pm 0.02$ [13]. Below, we will verify this procedure by the use of the modified AES treatment reported in several papers from this laboratory [14,18,19].

### 3.2. AES characterization of the ruthenium adlayers

The transfer of the clean Pt(111) electrode from UHV to 0.1 M $HClO_4$ solution and back to UHV (an "emersed" surface) was routinely performed without carbon contamination. As shown in figure 3A, the Auger secondary electron spectra indicate that the only surface elements after the emersion are platinum, chlorine and oxygen, that is, the substrate atoms and the constituents of adsorbed (and beam damaged [19]) perchloric acid, respectively. When the clean perchloric acid solution was replaced by the $5 \times 10^{-5}$ or $5 \times 10^{-4}$ M $RuCl_3$ solution (in 0.1 M $HClO_4$), and the electrode was withdrawn to UHV after 2 min of exposure to one of these solutions, the rest potential stabilized at 0.880 V, and a new AES peak at 274 eV became visible in addition to those from chlorine and oxygen

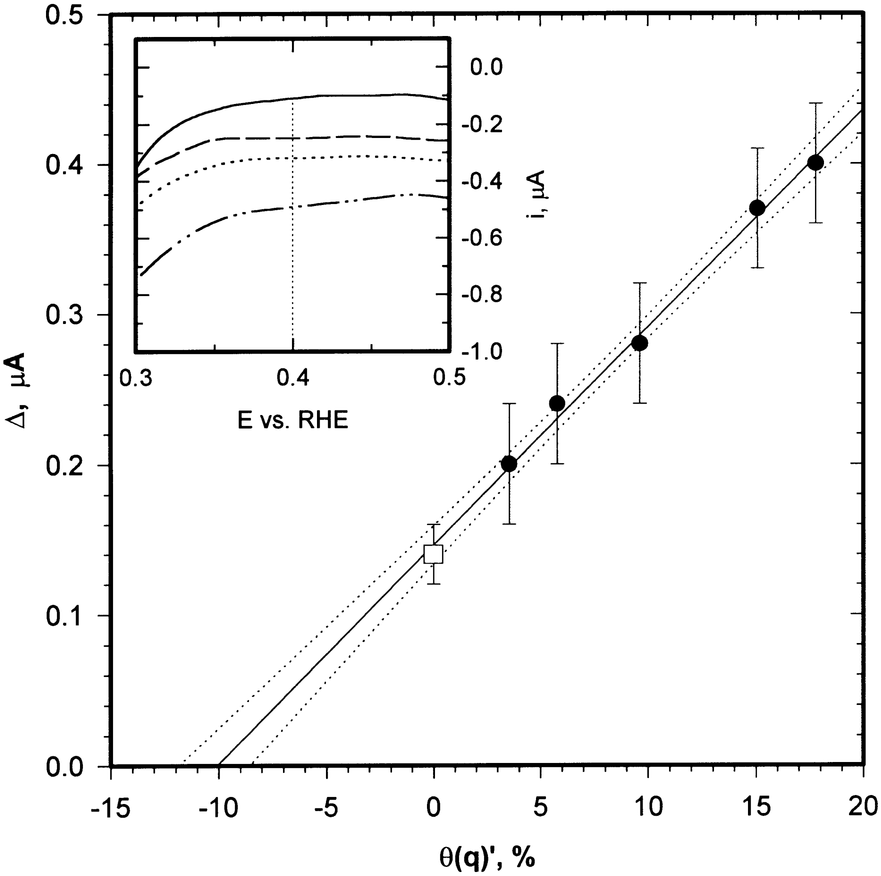

Figure 2. Electrochemical determination of the amount of spontaneous Ru deposit from $5 \times 10^{-5}$ M $RuCl_3$ + 0.1 M $HClO_4$ on Pt(111) using the current density expressed as Δ (see text) at 95% confidence level. Inset demonstrates how Δ was measured (from the solid line down) for four selected surfaces: clean Pt(111), the spontaneous Ru deposit at 10%, electrochemical Ru deposits, 14% and 28%.

(figure 3B). The new peak at 274 eV is due to the *spontaneously obtained ruthenium* species, as expected from the electrochemical study. We assign this peak to surface ruthenium rather than to carbon-containing impurities based upon the following observations.

(1) The AES peak position differs from that measured on C-contaminated surfaces (272 eV) by 2 eV.

(2) The 274 eV AES signal strength increased by a factor of 2 when more concentrated solution ($5 \times 10^{-4}$ M $RuCl_3$ in 0.1 M $HClO_4$) was used for the spontaneous deposition experiment (figure 3C).

(3) Annealing to ca. 450°C without or with oxygen at $3 \times 10^{-7}$ Torr did not lead to the 274 eV peak disappearance, as it does in the case of carbon contaminants. Instead, the peak increased roughly by 15% (and the relative signal of ruthenium vs. platinum, Ru/Pt, by 6%, see below) due to the desorption of surface chlorine and oxygen to vacuum, and a concomitant drop in the attenuation of Auger electrons from ruthenium and platinum (figure 3D).

Using the AES spectroscopic data, the packing density of the Ru species obtained from the spontaneous deposition was evaluated and compared to the electrochemical data presented above. For the AES calibration purpose two substrates were mounted close to each other on the UHV-electrochemistry manipulator [14]: a thick (several micrometers) ruthenium film deposited on the Pt(111) surface and the clean Pt(111) crystal. The secondary electron spectra were measured from the two surfaces: clean and covered by a monolayer of adsorbed perchlorate, to provide necessary entries for the quantitative determination of ruthenium. In essence, the comparison was made of the peak-to-peak (p/p) ratio of ruthenium at 274 eV relative to the Pt p/p ratio at 237 eV, denoted below as $I_{Ru}$ and $I_{Ru,0}$, respectively, using the equations presented below [18–20].

All measurements were conducted at 3 keV primary electron energy, $E_b$. The master equation in the packing density formula is

$$\frac{I_{Ru}}{I_{Ru,0}} = \frac{M_{Ru}}{M_{Ru,0}} \frac{r_{Ru}}{r_{Ru,0}} \frac{\lambda_{Ru}}{\lambda_{Ru,0}} [1 - \exp(-t/\lambda_{Ru} \cos\alpha)] , \qquad (2)$$

where $I_{Ru}$ and $I_{Ru,0}$ are the intensities of Ru(MNN) Auger transitions ($E = 274$ eV) in the Ru overlayer (on platinum) and in pure ruthenium, respectively, $M_{Ru}$ and $M_{Ru,0}$, in $1/cm^3$, are the mean atomic densities of ruthenium in the overlayer and in pure ruthenium, respectively, and $r_{Ru}$ and $r_{Ru,0}$ are the corresponding backscattering factors evaluated using the Ichimura et al. treatment [21]:

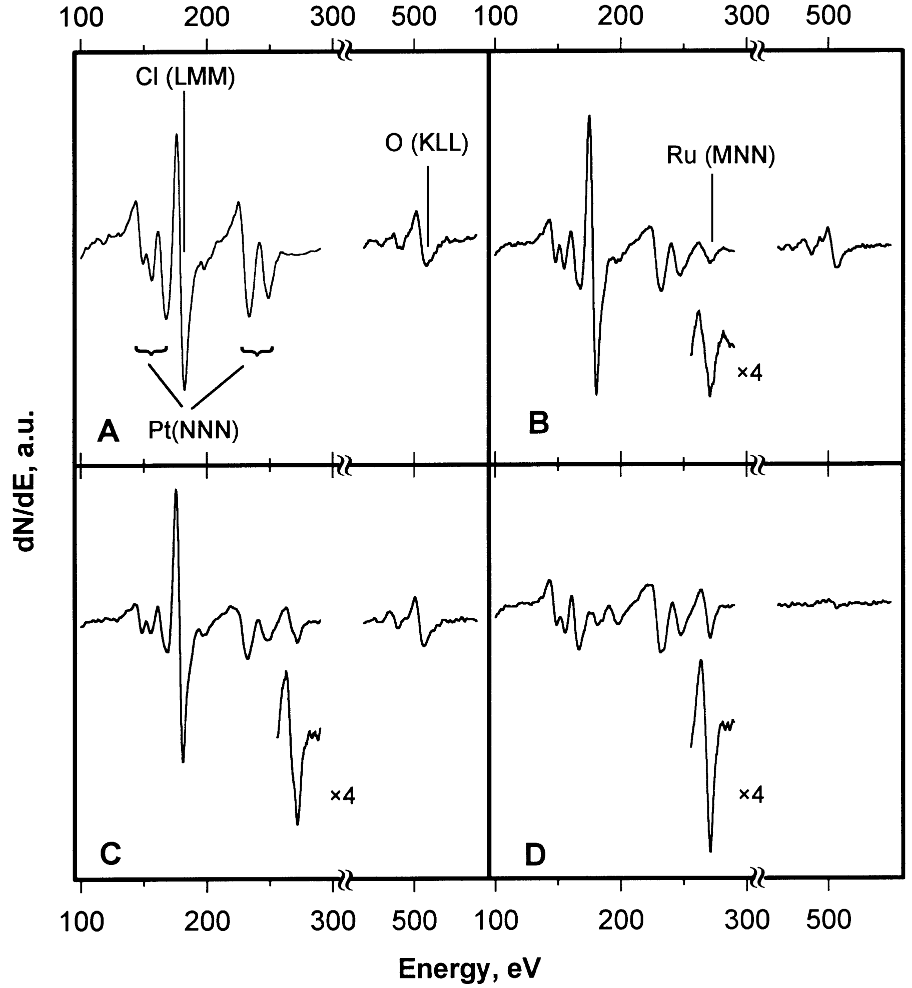

Figure 3. Secondary Auger electron spectra of the Pt(111) electrode: (A) The Pt(111) surface emersed from 0.1 M $HClO_4$ solution (a "clean surface"). (B) The Pt(111) surface covered by the Ru spontaneous deposit obtained in $5 \times 10^{-5}$ M $RuCl_3$ + 0.1 M $HClO_4$ during 2 min. (C) The Pt(111) surface covered by the Ru deposit obtained in $5 \times 10^{-4}$ M $RuCl_3$ + 0.1 M $HClO_4$ during 2 min. (D) The Auger electron spectrum as in figure 1C after 1 min annealing in UHV at approximately 450 C. Other experimental conditions were: primary beam energy: 3 keV, beam current 3 $\mu$A, p/p modulation amplitude 3 eV, lock-in amplifier time constant 3 ms. Data acquisition was carried out using custom-made software and a 386 PC.

$$r = 1 + (4.35 - 3.93Z^{0.1})(E_b/E)^{-0.25} + (4.85Z^{0.1} - 5.45)\,, \qquad (3)$$

where $Z$ is the atomic number of ruthenium and platinum, 44 and 78 respectively.

Further in equation (2), $\lambda$ is the inelastic mean free path (IMFP) of Auger Ru(MNN) electrons in the overlayer and in pure Ru, $t$ is the overlayer thickness, and $\alpha$ is the electron escape angle in CMA, 42.3°. The $\lambda$ values were estimated according to Tanuma et al. [22,23]:

$$\lambda = \frac{E}{E_p^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]}\,, \qquad (4)$$

where $E_p$ is the free-electron plasmon energy (in eV). Its value as well as those of the parameters $\beta$, $\gamma$, $C$, $D$, and the auxiliary variable $U$ were calculated using the following equations:

$$E_p = 28.8U^{1/2}\,, \qquad (5)$$

$$U = N_v\rho/A\,, \qquad (6)$$

$$\beta = -0.0216 + 0.944/E_p + 7.39 \times 10^{-4}\rho\,, \qquad (7)$$

$$\gamma = 0.191\rho^{-0.50}\,, \qquad (8)$$

$$C = 1.97 - 0.91U\,, \qquad (9)$$

$$D = 53.4 - 20.8U\,, \qquad (10)$$

where $N_v$ is number of valence electrons per Ru atom, and $\rho$ is macroscopic density, 12.3 g/cm$^3$ for pure ruthenium (or $\rho = M_{Ru}A$ in the surface ruthenium), and $A$ is the ruthenium mass number.

The final two-dimensional atomic packing densities ($m_{Ru}$, 1/cm$^2$) are obtained from

Table 1
Packing density of spontaneously deposited ruthenium from the quantitative AES measurements (first and second columns). Relative intensities of ruthenium 274 eV peaks for spontaneously deposited ruthenium (third column). Errors are given as confidence intervals at 95% confidence level

| Concentration (mol/ℓ) | Packing density (%) | | $I_{\mathrm{Ru}}$ [a] Ru(O/Cl) on Pt |
|---|---|---|---|
| | Ru(O/Cl) on Pt (uncorrected) | Ru(O/Cl) on Pt (corrected) | |
| $5 \times 10^{-5}$ | $9.4 \pm 1.4$ | $9.9 \pm 1.5$ | 0.372 |
| $5 \times 10^{-4}$ | $17.3 \pm 3.4$ | $18.2 \pm 3.6$ | 0.713 |

[a] $I_{\mathrm{Ru}}$ is the ratio of p/p Ru 274 eV intensity to p/p Pt 237 eV intensity. For all data $I_{\mathrm{Ru},0} = 11.44$.

$$m_{\mathrm{Ru}} = \frac{M_{\mathrm{Ru}}}{M_{\mathrm{Ru},0}} \frac{t}{t_0} \frac{m_{\mathrm{Ru},0}}{m_{\mathrm{Pt}}}\,, \tag{11}$$

where $M_{\mathrm{Ru}} = t^{-3}$ (as above, the ruthenium atomic density in the overlayer, $1/\mathrm{cm}^3$), and $M_{\mathrm{Ru},0} = t_0^{-3}$, the mean Ru atomic density in pure Ru ($1/\mathrm{cm}^3$), $m_{\mathrm{Ru},0} = M_{\mathrm{Ru},0} t_0$ is the ruthenium mean atomic density per plane ($1/\mathrm{cm}^2$) in pure Ru, $m(\mathrm{Pt}) = 1.51 \times 10^{15}$ ($1/\mathrm{cm}^2$) is the mean density of platinum atoms in the Pt(111) plane.

The application of equation (2) to the emersed Pt/Ru surface, that is, when oxygen and chlorine were present, causes the amount of ruthenium to be underdetermined (since the *attenuation* of the secondary electrons of platinum and ruthenium by chlorine and oxygen is unaccounted for (table 1, first column)). However, the correction for the signal attenuation by the Cl/O layer was obtained using the experimentally determined attenuation factors for ruthenium and platinum:

$$\frac{I_{\mathrm{Ru},0}(\mathrm{Cl/O})}{I_{\mathrm{Ru},0}}\,, \tag{12a}$$

$$\frac{I_{\mathrm{Pt},0}(\mathrm{Cl/O})}{I_{\mathrm{Pt},0}}\,, \tag{12b}$$

where $I_{\mathrm{Ru},0}(\mathrm{Cl/O})$ and $I_{\mathrm{Pt},0}(\mathrm{Cl/O})$ are the p/p intensities measured from the Cl/O-covered ruthenium (274 eV) and Pt (237 eV) electrodes, respectively, and $I_{\mathrm{Ru},0}$ and $I_{\mathrm{Pt},0}$ are the same intensities measured on the clean surfaces ($I_{\mathrm{Ru},0}(\mathrm{O,Cl})/I_{\mathrm{Ru},0} = 0.907$ and $I_{\mathrm{Pt},0}(\mathrm{O,Cl})/I_{\mathrm{Pt},0} = 0.953$). Dividing (12a) by (12b) gives the correction factor 0.952 by which the right-hand side of eq. (2) was multiplied. The corrected packing density data are given in the second column of table 1. (For the sake of completeness, the relative ruthenium intensities, $I_{\mathrm{Ru}}$, are given in the third column of table 1.)

For the $5 \times 10^{-5}$ M $\mathrm{RuCl_3}$ solution, the packing density, table 1, second column, can be compared to that obtained from electrochemistry, $\theta_0 = 0.10 \pm 0.02$. The data are in an excellent agreement. Using the $5 \times 10^{-4}$ M $\mathrm{RuCl_3}$ solution, the corresponding packing density obtained from AES measurements is $18.2 \pm 3.6$, table 1, second column. Interestingly, for the sample emersed from the $5 \times 10^{-4}$ M $\mathrm{RuCl_3}$ solution, and annealed for 1 min at ca. 450°C (figure 3D), the packing density is $17.8 \pm 3.4\%$, in a good agreement with the Cl/O-covered sample ($18.2 \pm 3.6$). We may conclude that the heat treatment used for the Cl/O removal under our experimental conditions does not lead to alloying and dissolution of ruthenium in platinum that, for higher temperatures, has been reported [24].

### 3.3. Reactivity

We have found that the spontaneously obtained ruthenium deposit is catalytically active towards methanol dissolved in the supporting electrolyte (figure 4 and tables 2 and 3). In figure 4, the oxidation current at 0.490 V for the Pt(111)/Ru electrode (shown are current densities, mA $\mathrm{cm}^{-2}$ of the real electrode surface), and for the clean Pt(111) electrode, is plotted as a function of oxidation time from 1 s to 30 min (chronoamperometry). (Current–time profiles for other surfaces – as basically similar – are not shown.) The *ruthenium enhancement*, defined as the current ratio due to methanol oxidation with and without ruthenium on the surface (table 2), is in the range of the previous values obtained with polycrystalline platinum/ruthenium alloys [10–12]. One notices that the oxidation current for Pt(111)/Ru is much higher than that for Pt(111) in the entire time span. At the end of the current–time profile, the rate of current decay is very low, confirming that the quasi steady-state oxidation conditions have been obeyed. For all crystals, the enhancement is low at the experiment beginning and

Table 2
Methanol oxidation at 0.490 V (vs. RHE) on Ru films spontaneously deposited on the Pt(111), Pt(110) and Pt(100) electrodes. Current density (mA $\mathrm{cm}^{-2}$) at the Ru-covered surfaces and ratio = ruthenium enhancement: the ratio of current due to methanol oxidation with and without ruthenium on the surface

| Time (s) | Pt(111)/Ru | | Pt(110)/Ru | | Pt(100)/Ru | |
|---|---|---|---|---|---|---|
| | $i$ (mA $\mathrm{cm}^{-2}$) [a] | ratio | $i$ (mA $\mathrm{cm}^{-2}$) [a] | ratio | $i$ (mA $\mathrm{cm}^{-2}$) [a] | ratio |
| 5 | 0.14 | 1.0 | 0.11 | 1.1 | 0.034 | 0.6 |
| 30 | 0.10 | 3.6 | 0.10 | 1.3 | 0.015 | 2.1 |
| 600 | 0.065 | 12 | 0.055 | 1.7 | 0.009 | 13 |
| 1800 | 0.047 | 15 | 0.038 | 2.5 | 0.006 | 15 |

[a] Per real surface area.

Table 3
Methanol reactivity on ruthenium films spontaneously deposited on Pt(111), Pt(110) and Pt(100) electrodes at 0.490 V: total charge during 30 min of reaction, the number of methanol monolayers reacted, and turnover numbers

| | Pt(111)/Ru | Pt(110)/Ru | Pt(100)/Ru |
|---|---|---|---|
| charge in 30 min (mC/cm$^2$) [a] | 113 | 96 | 16 |
| ML reacted in 30 min [b,c] | 226 | 311 | 37 |
| turnover numbers [d] (molecule s$^{-1}$ site$^{-1}$) | $3.1 \times 10^{-2}$ | $4.1 \times 10^{-2}$ | $5 \times 10^{-3}$ |

[a] Per real surface area.

[b] Assuming 3 surface sites per 1 methanol molecule.

[c] Numbers of centers per cm$^2$ are $1.5 \times 10^{15}$, $9.2 \times 10^{14}$ and $1.3 \times 10^{15}$ for Pt(111), Pt(110) and Pt(100), respectively.

[d] The current at 30 min is taken as a steady-state current.

quite large at the experiment end. For Pt(111)/Ru and Pt(100)/Ru, the enhancement approaches 15 at 30 min. For Pt(111), Pt(110) and Pt(100), the steady-state current is in the order of 0.047, 0.038 and 0.006 mA cm$^{-2}$, respectively. Apparently, as mentioned above, the Pt(111)/Ru is the most active surface. However, since the amount of the spontaneously deposited ruthenium varies from one crystal face to another: 0.10, 0.05 and 0.24 for Pt(111), Pt(110) and Pt(100) [13], the data do not yet directly relate to surface structure effects in methanol oxidation on the well-ordered Pt/Ru catalyst. Details of this issue will soon be provided [7]. Notably, the increase in ruthenium enhancement from 5 s to 30 min is accompanied by the drop in current density by a factor of up to 5.5 (table 2). The origin of this drop will be investigated elsewhere.

As shown in table 3, first row, the total charge involved in methanol oxidation is high for all surfaces. The magnitude of this charge indicates that much more than a monolayer of methanol reacted to $CO_2$ at 30 min, namely, 226, 311, and 37 monolayers for Pt(111), Pt(110) and Pt(100), respectively (assuming that three Pt sites are engaged in oxidation of one methanol molecule, second row). The fact that many methanol monolayers reacted provides the basis for transformation of the steady-state current density (at 30 min) to turnover numbers [25]. These values (table 3, last row) are very low, but are much higher than those with clean platinum single-crystal surfaces investigated at this potential [3].

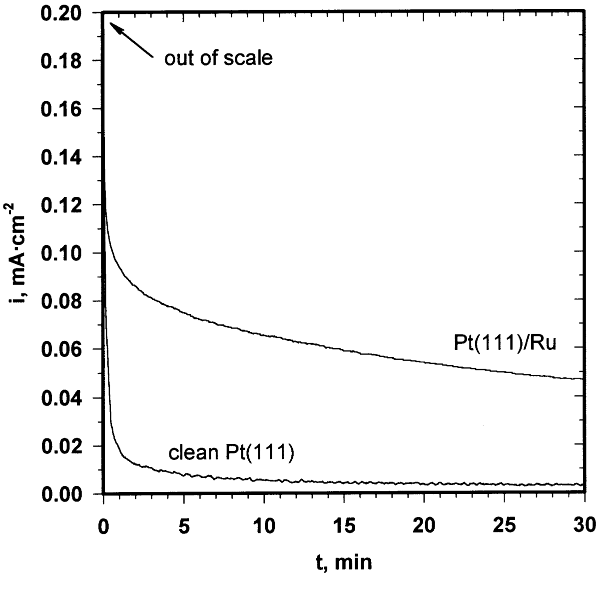

Figure 4. Current density vs. time plots at clean Pt(111) and Pt(111)/Ru (spontaneously deposited) electrodes from 1 s to 30 min at 0.490 V. Data were smoothed using a low pass numeric filter.

### 3.4. Mechanistic insights

The capability of ruthenium to nucleate oxygen-containing species at ca. 300 mV more negative potential than platinum are exploited in the so-called, *bifunctional mechanism* of methanol oxidation at Pt/Ru electrodes [9–12]. Within this mechanism, the sequence of the surface events is as follows: (i) an active ruthenium surface site is formed at an electrode potential of interest (Pt/$RuO_x$), (ii) surface CO is chemisorbed on a neighboring Pt site as a methanol poisoning species:

$$\mathrm{Pt} + \mathrm{CH_3OH} \rightarrow \mathrm{Pt{-}CO} + 4\mathrm{H}^+ + 4\mathrm{e} \qquad (13a)$$

(iii) oxygen is delivered from the Ru site to CO to form carbon dioxide:

$$\mathrm{Pt{-}CO} + \mathrm{Pt/RuO}_x \rightarrow \mathrm{Pt} + \mathrm{Pt/RuO}_{x-1} + \mathrm{CO_2} \qquad (13b)$$

(iv) the Pt/$RuO_x$ site is regenerated in reaction (14):

$$\mathrm{Pt/RuO}_{x-1} + \mathrm{H_2O} \rightarrow \mathrm{Pt/RuO}_x + 2\mathrm{H}^+ + 2\mathrm{e} \qquad (14)$$

with reaction (13a) re-starting on free Pt sites released from CO. The overall reaction therefore is

$$\mathrm{Pt/RuO}_x + \mathrm{CH_3OH} \rightarrow \mathrm{Pt/RuO}_{x-1} + \mathrm{CO_2} + 4\mathrm{H} + 4\mathrm{e} \qquad (13c)$$

with the total number of electrons per one methanol molecule equal to 6. Due to the oxidative properties of the more electronegative ruthenium, methanol decomposition on Pt/Ru electrodes occurs in the potential window suitable for methanol fuel cells [10–12].

Previous STM data demonstrate [26–28] that in the coverage range of interest to this study ruthenium is deposited on platinum as essentially two-dimensional islands of about 2–5 nm in diameter. This observation, together with the well-known result that ruthenium is inactive towards methanol at room temperature, and methanol creates CO on platinum easily (reaction (13a)), identifies the ruthenium island circumference as the site of reaction (13c). Adding to the comprehensive understanding of the ruthenium enhancement issue is our identification of the solution precursor of the spontaneously deposited ruthenium from perchloric acid media, namely, a hydrated ruthenyl, $RuO^{2+}$ or the aqua complex: $[RuO(H_2O)_4]^{2+}$ [29,30]. However, what is the chemical state of the spontaneously deposited ruthenium can only be tentatively proposed [13] and is being further examined in this laboratory.

## 4. Conclusions

Our findings are important for the following reasons. *First*, using the UHV spectroscopic evidence, we confirm that ruthenium is spontaneously deposited on platinum electrodes. *Second*, we determine the ruthenium packing density by the use of quantitative AES treatment. *Third*, we prove that such Ru deposits are catalytically active towards methanol dissolved in supporting electrolyte. At 30 min of the current measurement and for Pt(111) and Pt(100), the *ruthenium enhancement* factor (the current ratio due to methanol oxidation with and without ruthenium on the surface) is as high as 15. This compares favorably with previous literature data on polycrystalline Pt/Ru alloys. *Fourth*, since the steady-state currents and related rate data differ among platinum single-crystal faces examined, we begin to access surface structure effects in ruthenium-enhanced methanol oxidative electrocatalysis under quasi steady-state conditions. This work continues and more data of the type presented in this article will be available shortly.

## Acknowledgement

This work is supported by the National Science Foundation, under grant No. CHE 97-000963 and by the Department of Energy, grant DEFG02-96ER45439, administered by the Frederick Seitz Materials Research Laboratory at the University of Illinois.

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