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Surface X-ray scattering studies of the growth of Pd thin films on the Pt(001) electrode surface and the effects of the adsorption of CO

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Abstract

The morphology of electrochemically deposited Pd films on the Pt(001) electrode surface has been examined through the combination of cyclic voltammetry (CV) and in situ surface X-ray scattering (SXS). Analysis of SXS measurements has indicated that the Pd grows via pseudomorphic island formation, with the partial occupation of successive layers occurring at a first layer occupation of 0.8 ML. Further Pd deposition sees the formation of larger islands built onto the now complete monolayer, characteristic of pseudomorphic Stranski–Krastanov (SK) growth. In the H_{UPD} potential region the effect of CO on the surface expansion of the multilayer Pd film is negligible. In the hydrogen evolution region, however, the effect of the adsorption of CO has been shown to produce surface normal expansion and in-plane disorder of the Pd film. It is suggested that hydrogen permeation into the Pd film is enhanced on the CO-poisoned surface. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Developments in surface science spectroscopic techniques and UHV technology have, in recent years, provided the impetus for extensive experimental and theoretical study into adsorption phenomena on single crystal metal surfaces. Of particular interest from a catalysis/electrocatalysis standpoint are bimetallic surfaces whose catalytic

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properties vary greatly from the bulk metal counterparts and have been shown to be excellent surfaces for catalysing the oxidation of small organic molecules and CO. In the case of CO it has been shown that the Pt–CO bond is very strong and thus can poison active Pt sites [1–9]. This has led to the development of many bimetallic catalysts which are able to oxidatively remove CO from the surface at much more negative potentials than on Pt: representative examples are Pt–Ru, Pt–Mo. In contrast, for Pt modified with thin metal films of Pd, despite apparently easier OH adsorption [10], the oxidation of CO occurs at higher potentials [11,12].

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The growth of Pd on Pt(hkl) single crystal surfaces has been well documented in recent years [13-17] and on Pt(001) the formation of the second layer was observed to commence before the completion of the first [15]. Whereas the catalytic significance of the Pt(001)-Pd surface has been demonstrated with regard to the oxidation of formic acid, for example in Ref. [18], to our knowledge, little has been published on the effects of CO adsorption and oxidation regarding this surface. Electrochemically deposited Pd on the Pt(111) surface has been shown to grow via pseudomorphic Stranski-Krastanov (SK) growth whereby a complete Pd monolayer is formed before the onset of three-dimensional island formation [19].

In this paper we describe the growth of electrochemically deposited Pd films on the Pt(001) electrode surface. In Section 3.1, the voltammetric profiles from the Pt(001)-Pd surface over the range of coverage are discussed. In order to gain insight into the atomic structure of the Pd film, SXS measurements from the Pt(001)-Pd "1 ML" and "n ML" surfaces (a notation used to describe the Pd film in the high coverage regime, i.e. the coverage equivalent of several Pd monolayers, $n \ge 2$) are presented in Section 3.2. These two regimes are initially defined by the approximate Pd coverage inferred from the CV curves from the Pt(001)-Pd surface, the precise level of coverage is determined by the analysis of the crystal truncation rods (CTRs) measured from the surface. In Section 3.3, we present data for the multilayer film during the adsorption and oxidation of CO. These results indicate that the adsorption of CO on the multilayer Pd film appears to enhance the absorption of hydrogen into the Pd lattice.

2. Experimental details

Before each experiment the Pt(001) single crystals (miscut ~0.2°) were prepared using the flame annealing method and cooled in a hydrogen atmosphere (for details regarding the flame annealing method, see Ref. [20]). A droplet of ultrapure water was placed on the surface during transfer to an electrochemical cell to prevent any contamination. The surface was then immersed in 0.05 M H₂SO₄ (Baker, Ultrex) containing 10⁻⁵ M PdO (Alfa Products), the Pd being deposited while sweeping the potential at 20 mV s^{-1} . The amount of Pd on the surface was controlled by the continuous change of the voltammetric features associated with Pd deposition [15,21]. Once the approximate coverage had been attained, the Pd modified Pt electrodes were removed, rinsed with water and transferred to the X-ray cell containing 0.05 M H_2SO_4 free from Pd^{2+} ions. The SXS measurements were performed on a four-circle goniometer on beamline 7.2 at the Stanford Synchrotron Radiation Laboratory (SSRL) using a monochromatic incident X-ray beam of energy 10 keV defined by slits to be a $1 \times 1 \text{ mm}^2$ spot at the sample. For the experiments involving CO, the outer shell of the X-ray cell was purged with CO (99.99% purity) instead of N_2 , which is usually used to prevent contamination of the electrode by the atmosphere. CO is able to saturate the solution because it can diffuse through the polypropylene film used to trap the electrolyte (further details regarding the X-ray cell can be found in Ref. [22]). The reciprocal space notation used is for the surface tetragonal unit cell for the (001) surface, which is related to the conventional cubic cell by the transformations $(1,0,0)_t = 1/2(2,-2,0)_c$, $(0,1,0)_t = 1/2(2,2,0)_c, (0,0,1)_t = (0,0,1)_c.$ All electrode potentials are quoted versus a Pd/H₂ reference electrode to an accuracy of ± 0.05 V.

3. Results and discussion

3.1. Cyclic voltammetry

The voltammetric response from the Pt(001)– Pd surface has been well documented [15,21] and is shown in Fig. 1(a). In agreement with previous work, the base voltammetry of Pt(001) (n = 0) shows three separate potential regions: the pure H_{UPD} region (0.1 V < E < 0.23 V) is followed first by H_{UPD} desorption/adsorption and bisulfate adsorption/desorption (0.23 V < E < 0.41 V) and then by the double layer potential region (E > 0.48V). The voltammetric profile from the Pt(001)–Pd ML surface (Fig. 1(a) ($n \approx 1$)) sees the emergence



Fig. 1. (a) Cyclic voltammetry from the Pt(001) and Pt(001)–Pd surface in 0.05 M H₂SO₄ at a sweep rate of 20 mV s⁻¹. Subsequent to Pd deposition, sharp peaks arise at \sim 0.2 and 0.29 V which correspond to surface adsorption sites and step sites respectively. The 0.29 V peak is due to adsorption/desorption at Pt and Pd step sites, which occur before the completion of the monolayer. (b) A schematic of the Pt(001)–Pd surfaces derived from the CTR measurements at each level of Pd coverage.

of two main features. The first peak at ≈ 0.2 V corresponds to H_{UPD} adsorption/desorption accompanied by bisulfate desorption/adsorption from the pseudomorphic Pd monolayer (see Section 3.2). The second peak at ≈ 0.29 V also corresponds to H_{UPD} desorption/adsorption with concurrent bisulfate adsorption/desorption. but from the small number of Pd islands formed on the top of the first Pd layer. A close inspection of Fig. 1(a) shows that there is also current in the potential range of 0.3 V < E < 0.45 V, which is most likely due to H_{UPD} desorption/adsorption from Pdfree Pt atoms. Thus, the voltammetric studies indicate that formation of the second layer of Pd commences prior to the completion of the first. The voltammetry from the Pt(001)-Pd n ML surface is illustrated in Fig. 1(a). Notice that depositing more than 1 ML of Pd produces voltammetry in which the peak at 0.29 V is becoming predominant while the peak at 0.2 V is hardly visible. Furthermore, the fact that the pseudocapacitance observed between 0.3 V < E < 0.45 V on the surface covered by 1 ML of Pd is completely suppressed on Pt(001)–Pd modified by *n* ML indicates that for n > 2 all Pt atoms are covered with Pd, as illustrated in the model of Fig. 1(b) and discussed in more detail below.

3.2. CTR measurements

The CTR data taken from the Pt(001)–Pd ML surface with the potential held at 0.05 V are shown as circles in Fig. 2. The solid line is a fit to the data and the dashed line shows the scattering from an ideally terminated Pt(001)-(1×1) surface, a convention which is adopted throughout the paper.



Fig. 2. Non-specular CTRs from the Pt(001)–Pd ML surface taken at an electrode potential of 0.05 V. The circles represent the data; the solid line is a best fit to the data using a structural model which includes pseudomorphic Pd adlayers as described in the text. The dashed line is a calculation of the scattering from an ideally terminated Pt(001)-(1×1) surface. The CTRs are plotted as a function of the surface normal reciprocal lattice vector c^* .

Comparison between the data and the ideal calculation shows that the presence of adsorbed Pd produces a significant reduction in the scattered intensity midway between the Bragg reflections, at the so-called "anti-Bragg" positions. Here the intensity is dependent only on the surface layer of the Pt and any adsorbed overlayers because the scattering from the bulk Pt lattice cancels out. Since Pd has a lower atomic form factor than that of Pt, the presence of adsorbed Pd produces a large reduction in the scattered intensity. This effect is similar to that produced by a partially occupied surface Pt layer. The structural model used to reproduce these data included a variable number of partially filled pseudomorphic Pd adlayers, with a coverage θ_{Pd} per Pt atom. Other structural parameters were the relaxation of the topmost Pt atomic layer from the bulk position, ε_{Pt} , the Pt–Pd and Pd–Pd surface normal spacing, d_{Pt-Pd} and d_{Pd-Pd}, and a Debye-Waller type r.m.s. roughness of the surface of the Pt electrode and the Pd adlayer, σ_{Pt} and σ_{Pd} respectively. In order to detect any incommensurate Pd structures, radial scans were performed at the reciprocal lattice position (1, 0, 0.1). These scans showed no evidence of peak splitting within the resolution of the experiment, indicating that the Pd is lattice matched in the surface plane to the Pt substrate, i.e. the growth is pseudomorphic. Therefore, the model assumes the Pd to be adsorbed at fourfold hollow sites to continue the fcc stacking of the bulk lattice. Including Pd atoms at other adsorption sites gave calculated CTRs that were not consistent with the measured data. The results from the best fit gave an occupation of the first Pd layer, $\theta_{Pd1} = 0.8 \pm 0.1$ ML with an occupation of the second Pd layer of $\theta_{Pd2} = 0.15 \pm 0.1$ ML, as predicted by the electrochemical measurements. The Pt–Pd layer spacing, $d_{Pt-Pd} = 2.00 \pm 0.01$ Å, corresponds to an expansion of $\sim 2\%$ of the bulk Pt(001) spacing (1.96 Å) which is similar to that measured for the clean Pt(001) surface covered by a ML of adsorbed H_{UPD} [23]. The fractional occupation of the Pd adlayers provides the necessary Pd step sites to produce a large contribution to the voltammetry peak at 0.29 V. A schematic of the Pt(001)-Pd ML surface is shown in Fig. 1(b).

Fig. 3 shows the CTRs measured from the Pt(001)-Pd n ML surface, measured at an electrode potential of 0.05 V. The model used to describe the multilayer employed a half-Gaussian distribution of layer occupation. The Gaussian was essentially a half distribution built on top of a variable number of full layers, the peak of the distribution being the layer with greatest occupancy (for more details on the model see Ref. [19]). The results from the best fit (solid line) give a complete monolayer, with an occupation of 1.0 ± 0.1 ML on top of which three-dimensional island formation has taken place. The Pt-Pd layer spacing is slightly contracted from that of the Pt(001) bulk spacing at $d_{Pt-Pd} = 1.93 \pm 0.01$ Å, which is close to the bulk Pd(001) spacing of 1.94 A. The Pd within the islands has a surface-normal lattice spacing of 1.95 ± 0.01 Å i.e. also equal to the



Fig. 3. Non-specular CTRs from the $Pt(0\ 0\ 1)$ –Pd *n* ML surface taken at an electrode potential of 0.05 V. The circles represent the data taken, the solid line is a best fit to the data using a structural model which describes a half-Gaussian distribution of layer occupation for pseudomorphic layers of Pd as described in the text. The dashed line is scattering calculated from an ideally terminated $Pt(0\ 0\ 1)$ -(1×1) surface. The CTRs are plotted as a function of the surface normal reciprocal lattice vector c^* . Inset: A plot of the Pd layer occupancy derived from the half-Gaussian distribution.

bulk Pd(001) spacing. The Pd multilayer reaches a total of seven partially occupied Pd layers. Fig. 1(b) shows a schematic of the Pt(001)-Pd *n* ML thin film structure.

In a previous publication, we have shown that Pd films grow via pseudomorphic Stranski–Krastanov growth on the Pt(111) surface with threedimensional islands described by a half-Lorentzian distribution of layer occupation [19]. Here our results show that, while it may not be true SK growth, Pd films grow in much the same manner on the Pt(001) surface i.e. via pseudomorphic island formation. The main differences between the two substrate orientations are that on the Pt(001) surface the formation of the second layer begins before the completion of the first and with further deposition, the formation of three-dimensional islands occurs. The SXS results provide strong evidence in support of the assignment of the various features in the voltammetric profiles recorded from both the clean Pt(001), and the Pt(001)–Pd surface at the two levels of Pd coverage: the ≈ 0.2 V peak due to Pd terrace sites is greatly suppressed at higher coverage; the ≈ 0.29 V due to Pd step sites dramatically *increases* with higher coverage (which suggests island formation); the feature associated with Pt terrace sites is not present at higher coverage (which suggests that the Pt surface is completely covered by Pd).

3.3. Adsorption of CO

To investigate the influence of CO adsorption on the Pt(001)-Pd n ML surface, once the CTR measurements had been taken, the electrolyte in the X-ray cell was saturated with CO with the potential being held at 0.05 V (in the H_{UPD} region). During saturation of the electrolyte with CO the X-ray intensity was monitored at (1, 0, 2.73), a position sensitive to lattice expansion in the Pd film. No changes were observed in the X-ray intensity, although H_{UPD} is displaced from the Pd surface by CO. This implies that there is no significant change in the thin film structure although it is not possible to rule out an expansion of the Pd surface atoms. Sweeping the potential into the hydrogen evolution region (-0.04 V), however, led to a dramatic decrease in the X-ray intensity at (1, 0, 2.73). This is shown in Fig. 4(b) as the potential is cycled from -0.04 to ~ 0.6 V. It should be noted that a similar effect was not observed in CO-free electrolyte implying that CO adsorbed on Pd has a special effect on the Pd film structure in the hydrogen evolution region.

In order to characterize the structural changes, CTR data was measured at -0.04 V in CO-saturated electrolyte. As previous results suggest that Pd is not displaced from the Pt surface [12], in order to fit the CTR data, the same structural model was used as for the Pt(001)–Pd *n* ML surface free from CO. Due to the scattering power of CO relative to Pd and Pt, it us unnecessary to



Fig. 4. (a) CV from the Pt(001)–Pd *n* ML surface in 0.05 M H₂SO₄ at a sweep rate of 20 mV s⁻¹. (b) XRV at the reciprocal lattice position (1, 0, 2.73), a position sensitive to the expansion of the lattice. (c) Rocking scans through the (1, 0, 2.73) position. The data taken before the introduction of CO are represented by circles, the triangles are data taken subsequent to saturation of the electrolyte with CO. The solid lines are fits of a Lorentzian lineshape to the data.

include CO in the structural model. The only parameters allowed to vary were the inter layer spacings, d_{Pt-Pd} and d_{Pd-Pd}, and the relaxation of the top most Pt layer. All other parameters were fixed at the values obtained from the fit to the Pt(001)-Pd n ML data. The results from the fit show that the introduction of CO causes a significant expansion ($\sim 3\%$) of both the Pd–Pd spacing in the Pd film and the Pt-Pd layer spacing. This dramatic expansion of the Pd lattice is illustrated by the plot in Fig. 5 which shows the ratio of intensities along the non-specular CTRs before and after the introduction of CO, I and I_{CO} respectively. The fit to this ratio data set is essentially a three parameter fit, only allowing for the expansion of the Pd lattice and relaxation of the Pt surface layer.

The CTR analysis indicates that the Pd expansion is caused by CO-induced hydrogen absorption into the Pd lattice. Further evidence for this can be seen in Fig. 4(a) and (b), which show the CV and XRV measurements. Similarly to the Pt(111)–Pd surface [19], the introduction of CO has no effect on the expansion in the H_{UPD} region. A significant lattice expansion occurs over the range -0.04 to 0.05 V, which coincides with the potential region of the hydrogen evolution reaction (HER). Furthermore, Fig. 4(c) shows rocking scans performed at (1, 0, 2.73) before (circles) and after (triangles) saturation of the electrolyte with CO. Fits of a Lorentzian lineshape of the data are shown as solid lines. At this reciprocal lattice position, the X-ray intensity is dominated by scattering from the Pd film, therefore the FWHM of these scans are inversely proportional to the inplane ordering of the Pd film. The domain size was calculated from the values obtained for the FWHM of the Lorentzian fit. The fits gave domain sizes of \sim 220 A (without CO) and \sim 201 A (with CO). Therefore the introduction of CO has led to a reduction of the in-plane domain size by $\sim 8.5\%$, indicative of a distortion of the Pd lattice. This distortion is probably caused by the presence of interstitial hydrogen. With this limited data set it is impossible to propose a detailed mechanism for the observed lattice expansion. It is interesting,



Fig. 5. Plot of the ratio, $R = I_{CO}/I$, of the intensities along the non-specular CTRs measured from the Pt(001)–Pd *n* ML surface before (*I*) and after (I_{CO}) the introduction of CO with the potential held at -0.04 V, plotted as a function of the surface normal reciprocal lattice vector c^* . These show large fluctuations around the Bragg reflections at (1, 0, 1), (1, 0, 3) and (1, 1, 2) indicative of significant changes in the layer spacing within the lattice. The solid line is a fit to the data (see text for details).

however, that chemisorbed CO, similarly to elements that act as surface poisons to the HER (such as P, S, As, Se, Sb) [24], is able to promote hydrogen absorption into the Pd film. Although there may be several explanations for this effect, this behaviour can be associated with the modification of physico-chemical properties of the Pd film. As previously proposed for the Pt(111)-S system [24], a promoting effect may related to the local surface electronic effects which give rise to electron transfer between adsorbed CO and H_{UPD} through the underlying metal.

4. Conclusions

The growth of electrochemically deposited Pd films on the Pt(001) electrode surface and the structural effects due to the adsorption of CO have

been studied. We have shown that Pd grows epitaxially via the formation of three-dimensional pseudomorphic islands, i.e. the Pd is lattice matched in-plane to the Pt substrate. These islands give rise to characteristic features in the voltammetric response from the surface. The CTR results show that for the Pt(001)-Pd 1 ML, the Pt-Pd spacing is expanded from the bulk Pt-Pt spacing by $\sim 2\%$ in the presence of a monolayer of H_{UPD}. This expansion is similar to that observed for the clean Pt surface [23]. With higher Pd coverage, the Pt-Pd spacing relaxes to the bulk Pt-Pt layer spacing. Similarly, the Pd film adopts the bulk Pd(001) lattice spacing. The growth mechanism of the Pd film is similar to that observed for Pd thin films on the Pt(111) surface [19], although for the Pt(001)-Pd system the formation of threedimensional islands begins to take place prior to the completion of the first monolayer. The adsorption of CO onto the Pt(001)-Pd multilayer surface produces significant surface normal expansion and in-plane distortion of the Pd lattice in the potential region of hydrogen evolution. It is postulated that this is due to enhanced absorption of hydrogen on CO-covered Pd films.

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References

 B. Beden, S. Blimes, C. Lamy, J.M. Leger, J. Electroanal. Chem. 149 (1983) 295.

- [2] S. Sun, J. Clavilier, A. Berwick, J. Electroanal. Chem. 240 (1988) 147.
- [3] L.-W. Leung, A. Wieckowski, M.J. Weaver, J. Phys. Chem. 92 (1988) 6985.
- [4] J.M. Orts, A. Fernandez-Vega, J.M. Feliu, A. Aldaz, J. Clavilier, J. Electroanal. Chem. 327 (1992) 191.
- [5] B.E. Hayden, A.J. Murray, R. Parsons, D.J. Pegg, J. Electroanal. Chem. 409 (1996) 51.
- [6] C.A. Lucas, N.M. Markovic, B.N. Grgur, P.N. Ross, Surf. Sci. 448 (2000) 65.
- [7] C.A. Lucas, N.M. Markovic, P.N. Ross, Surf. Sci. 448 (2000) 77.
- [8] M. Ball, C.A. Lucas, N.M. Markovic, B.M. Murphy, P. Steadman, T.J. Schmidt, V. Stamenkovic, P.N. Ross, Langmuir 17 (2000) 5943.
- [9] N.M. Markovic, B.N. Grgur, C.A. Lucas, P.N. Ross, Langmuir 16 (2000) 1998.
- [10] B. Alvarez, V. Climent, A. Rodes, J.M. Feliu, Phys. Chem. Chem. Phys. 3 (2001) 3269.
- [11] B. Alvarez, V. Climent, A. Rodes, J.M. Feliu, J. Electroanal. Chem. 497 (2001) 125.
- [12] C.A. Lucas, N.M. Markovic, M. Ball, V. Stamenkovic, V. Climent, P.N. Ross, Surf. Sci. 479 (2000) 241.

- [13] J. Clavilier, M.J. Llorca, J.M. Feliu, A. Aldaz, J. Electroanal. Chem. 310 (1991) 429.
- [14] G.A. Attard, A. Bannister, J. Electroanal. Chem. 300 (1991) 467.
- [15] M.J. Llorca, J.M. Feliu, A. Aldaz, J. Clavilier, J. Electroanal. Chem. 351 (1993) 299.
- [16] G.A. Attard, R. Price, A. Al-Akl, Electrochim. Acta 39 (1994) 1525.
- [17] M. Han, P. Mrozek, A. Wieckowski, Phys. Rev. B 48 (1993) 8329.
- [18] M. Baldauf, D.M. Kolb, J. Phys. Chem. 100 (1996) 11375.
- [19] M.J. Ball, C.A. Lucas, N.M. Markovic, V. Stamenkovic, P.N. Ross, Surf. Sci. 518 (2002) 201.
- [20] N.M. Markovic, M. Hanson, G. McDougal, E. Yeager, J. Electroanal. Chem. 214 (1986) 555.
- [21] G.A. Attard, R. Price, Surf. Sci. 448 (2000) 65.
- [22] I.M. Tidswell, N.M. Markovic, C.A. Lucas, P.N. Ross, Phys. Rev. B 47 (1993) 16542.
- [23] N.M. Markovic, C.A. Lucas, B.N. Grgur, P.N. Ross, J. Phys. Chem. B 103 (1999) 9616.
- [24] Y. Sung, W. Chrzanowski, A. Wieckowski, A. Zolfaghari, S. Blais, G. Jerkiewicz, Electrochim. Acta 44 (1998) 1019, and references therein.