# A STM Investigation of Pt-Single Crystal Surfaces in Air and Electrolyte Solutions

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We describe the construction of a beetle-type scanning tunneling microscope optimized for in situ measurements. The influence of the crystal preparation technique on the surface structure is reported. Whereas annealing of platinum single crystals in iodine vapour yields smooth surfaces for the low index faces, which are protected from contamination in air by the adsorbed iodine, facetting occurs in the case of stepped surfaces. – The iodine adlattices are resolved both in air and electrolyte: Pt(111) (3 × 3)-I and Pt(100) ( $\sqrt{2} \times 5\sqrt{2}$ )R 45°-I, thus confirming previous LEED results.

## Introduction

The importance of using single crystals for fundamental research in heterogeneous catalysis is generally accepted. Far less attention than to the metal gas interface has been paid for the study of the metal electrolyte interface. This is not only due to the difficulty of preparing well defined single crystal surfaces of the catalytically most active Pt-group metals outside of a UHV-chamber, but also to the nonapplicability of most surface sensitive analytical techniques. Major advances, however, have been achieved in recent years:

Ways of preparing single crystal Pt-electrodes outside of a UHV-chamber have been described [1-4]. Also, several spectroscopic methods have been developped which allow the in situ study of electrode surfaces (for reviews see [5,6]).

The importance of using single crystal surfaces is demonstrated by their different electrocatalytic activity, e.g., for the oxidation of formic acid [7]. Using differential electrochemical mass spectrometry (DEMS), we have recently shown for the case of benzene desorption, that also the product distribution depends on the surface structure [8].

For a thorough understanding of surface reactions on an atomic level, a detailed knowledge of both electrode and adsorbate structure is a prerequisite. The use of scanning tunneling microscopy for this purpose is especially intriguing, since this method is able to yield real space images of surfaces on an atomic level.

Several scanning tunneling microscopes suitable for in situ use have been described in the literature, but only in few cases an atomic resolution of adlattices was obtained, e.g. for underpotentially adsorbed Cu on Au(111) and (100) [9], iodine on Pt(111) [10], and, most recently, for CO on Rh(111) [11].

Three different ways of preparing clean and smooth Ptsingle crystal surfaces have been described, which all involve annealing the crystal by heating to redness as the first step: One method, originally used by Clavilier for small single crystal beads [1], involves quenching of the annealed crystal in ultrapure water. In order to avoid the thermal stress in the case of large crystals, Wieckowski et al. [2,3] developped a method according to which the hot Pt-electrode cools down in an atmosphere of inert gas saturated with iodine. The iodine adsorbs on the surface and protects it from contamination during the cooling and transfer to an electrochemical cell. Prior to the electrochemistry, however, the iodine has to be desorbed, which can be done either in alkaline solutions [8,12] or by replacing it with CO [3].

A third method involves cooling the hot single crystal in a hydrogen or argon stream and quenching it after reaching a temperature of 100-200 °C [4]. All problems with extreme thermal stress and difficulties in desorbing the iodine are avoided, but an extreme care has to be used to prevent any contamination during the cooling period, during which carbon impurities are no longer oxidized as in the case of the red-hot crystal.

The appropriateness of the preparation in iodine vapour has so far only been demonstrated for the (111) and (100) face of Pt and Rh [13,14] using both LEED for ex situ and UPD of Ag on these surfaces for electrochemical characterization. For Pt(111) it was also demonstrated by STM [15].

In this paper, we describe a new STM for use in electrochemistry, which is based on that described by Besocke [16,17] and which is very rigid and shows an extremely low drift. We present in situ recorded images showing adlattice structures of iodine adsorbed on Pt(111) and Pt(100).

# Experimental

Our homebuilt STM is designed to allow imaging of immersed samples under potential control. It is mounted as usual on a Viton damped stack of metal plates. The uppermost plate supports the sample and the STM base plate. The whole STM is mounted on a vibration isolation table and is enclosed in a plexiglas housing, which serves for thermal isolation and allows measurements under inert gas atmosphere.

The STM head itself (Fig. 1) is derived from the "beetle type" construction of Besocke et al. It was modified to minimize the number of electrical connections to the moving parts, and, of course, for use in electrochemistry. Its main parts are the scanner (1) with the tip, the scanner support disk (2), three outer piezos (3) which serve for coarse positioning and support this disk, and the electrochemical cell.

The cell (diameter 6 mm) consists of a KEL-F cylinder and a Kalrez O-Ring which are spring loaded against the sample surface. This gives a cell volume of 150  $\mu$ l. The sample can be easily exchanged by lifting the STM base plate. Electrolyte is introduced

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into this cell through a PTFE tube ending in a piece of Pt-tube, which is fixed at a PTFE cantilever. This Pt-tube also serves as counter electrode. The end of a small Pt-wire fixed in a bore of the KEL-F cylinder serves as a dynamic hydrogen reference electrode [18], see below.



## 5,

Fig. 1

- Modified "beetle-type" STM
- a) Perspective view of STM head
- b) Sectional view of the electrochemical cell
  (1) single tube scanner with tip (2) scanner support disk (ramp slider) (3) ball bearing carrier piezo (4) STM base plate (5) KEL-F cell (6) leaf spring (7) PTFE cantilever (8) fluid line (9) counter electrode (Pt-tube) (10) reference electrode (Pt-wire) (11) Kalrez o-ring (12) sample (13) sample support plate

The tip can be scanned in x, y directions by applying appropriate voltages to the four outer electrodes of the scanner piezo. For a vertical movement a voltage between all outer electrodes and an inner electrode is applied.

Coarse approach is achieved using the inertial slider principle:

The three ball bearing outer piezos which are glued onto the base plate of the STM and which support the scanner support disk, are quickly tangentially moved in one direction and slowly back to their original position. Due to inertia, the disk (2) does only follow the slow movement. Repeating this process results in a rotation of the disk. Ramps machined into this disk translate this rotation into a vertical movement of the scanner and hence the tip. This allows approaching and retracting of the tip to or from the sample, respectively.

For an evaluation of the piezo constants, a calibration is performed using HOPG graphite.

Our electronics constists of an I/V-converter which is incorporated in the STM head, the usual feeedback loop based on a logarithmic amplifier and an integrator, a digital scan generator and a  $\pm 100$  V final stage. A compensation voltage applied to the outer piezos prevents high DC levels at the scanner electrodes. Data acquisition and control of the instrument are performed by a PC 386-20 with STiMage software from RHK Technology, Rochester Hills, USA. Computer and electronics are interfaced via a DT 2821-F interface board from Data Translation, Marlboro, USA. The scan generator was designed to emulate the RHK STM 100-3 electronics from RHK Technology, Rochester Hills, USA. The circuitry is based on timing diagrams and communication protocol provided by RHK.

A homebuilt bipotentiostat and function generator are connected to the STM circuity by carefully avoiding ground loops. The potential of the reference electrode is defined to a few mV negative of the RHE by evolving a small amount of hydrogen (about 1  $\mu$ A) at the Pt wire. The tip potential can be controlled versus the working electrode (sample) or the reference electrode respectively.

With the tip referred to the reference electrode it is possible to image the electrode surface while the electrode potential is scanned, however it must be assured that the bias voltage  $V_{\rm B} = T_{\rm TIP} - V_{\rm SAMPLE}$  does not become zero while the STM feedback loop is active.

Tips were etched from a Pt/Ir wire (0.25 mm) and insulated with epoxy resin. The surface tension of the resin assures that the very tip remains uncoated [19]. Most of the coated tips showed ultramicroelectrode behaviour as checked by voltammetry in  $10^{-2}$  M solutions of Fe<sup>2+</sup>. From the limiting current of Fe<sup>2+</sup> oxidation we derived electrode surface areas of 10 µm<sup>2</sup> to 200 µm<sup>2</sup>, hemispherical diffusion assumed [19]. After annealing at 80 °C for two hours the epoxy coating was stable and clean enough to be no source of contamination in the electrochemical cell. This is shown by cyclic voltammetry of a polycrystalline Platinum electrode in 0.1 N H<sub>2</sub>SO<sub>4</sub> in the STM cell with immersed epoxy-coated tip (Fig. 2). This cyclic voltammogramm also shows, that we do have an inert atmosphere in the STM-cell.



#### Fig. 2

Cyclic voltammogramm of a polycrystalline Pt electrode in 0.1 N  $H_2SO_4$ , recorded in the STM cell with immersed epoxy-coated tip; sweep rate 50 mV/s

As samples we used Pt single crystals of four different orientations, all about 3 mm thick and 10 mm in diameter:

- a Pt(111), purchased from Goodfellow, Cambridge, UK, oriented and polished to within  $\pm 0.2^{\circ}$  by the KFA Jülich, FRG,
- a Pt(332), also purchased from Goodfellow and oriented to within  $\pm 2^{\circ}$ ,
- a Pt(110) oriented to within  $\pm 1^{\circ}$ , and a Pt(100) oriented to within  $\pm 0.25^{\circ}$  were purchased from Kristallhandel Kelpin, Leimen, FRG.

All single crystals were delivered with one side polished with 1  $\mu$ m diamond paste. All were cleaned by repeated oxidation –

reduction cycles in 1 N  $H_2SO_4$  and rinsed with Millipore water. Prior to STM experiments the sample was heated in a hydrogen flame to about 1000 K for a few minutes. The hot crystal was then transfered into a flask purged with nitrogen and containing some iodine crystals. For some experiments the Pt(110) and Pt(332) were cooled in pure nitrogen atmosphere and afterwards coated with iodine from a  $10^{-4}$  M solution of KI.

# Results

## The Topography

The typical topography of a Pt(111) electrode surface prepared in I<sub>2</sub> vapor is shown in Fig. 3. As already reported by Schardt [15], the surface consists of atomically flat terraces which are several hundred nm long and several ten nm broad. They are separated by steps which are between one and ten atomic layers high. Identical images were obtained in and ex situ.



## Fig. 3

Topographic image of Pt(111) immersed in  $10^{-4}$  M KI,  $10^{-2}$  M NaClO<sub>4</sub>,  $10^{-4}$  M HClO<sub>4</sub>; sample potential 0.5 V RHE, tip potential 0.75 V RHE; scan area 400 × 400 nm, scanning speed 200 nm/s



## Fig. 4

Topographic image of Pt(100) immersed in  $10^{-4}$  M KI,  $10^{-2}$  M NaClO<sub>4</sub>,  $10^{-4}$  M HClO<sub>4</sub>; sample potential 0.75 V RHE, tip potential 0.7 V RHE; scan area  $400 \times 400$  nm, scanning speed 200 nm/s

As expected, a similarly smooth surface is obtained in the case of the (100) face (Fig. 4). As we have already reported for the same surface in air [20], the large terraces are separated by monoatomic steps, which predominantly run along the (001) direction. The (110) face, prepared in iodine, looks rather rough at first sight (Fig. 5), exhibiting a structure of parallel ridges with varying height and width. Note, however, that the *z*-scale is only about 10 atomic layers.



#### Fig. 5

Topographic image of Pt(110) in air showing a  $(1 \times n)$  reconstruction; scan area  $200 \times 200$  nm, scanning speed 60 nm/s

At increased resolution, superimposed to these ridges smaller corrugations of atomic dimensions become visible (Fig. 6). Those we interpret as the well known missing rows of the  $(1 \times 2)$  reconstruction [21]. In the middle of Fig. 6 one row is larger than the others, the back part of the figure is, one the average, higher than the front part. We therefore believe that the fourth row is an extra atom high, corresponding to a local  $(1 \times 3)$  reconstruction or, in other words, to a phase boundary between islands of different height as seen before for the clean Pt(110) surface [22]. It is obvious that the existance of several of such steps lead to deeper valleys which run in a prediminated direction.



## Fig. 6

Topographic image of Pt(110) in air showing a  $(1 \times 2)$  reconstruction; scan area  $6 \times 6$  nm, scanning speed 100 nm/s

For the stepped Pt(332) the preparation in the iodine containing atmosphere leads to a highly facetted surface. The degree of facetting is sensitive to the exact parameters of preparation such as annealing temperature, speed of transfer and nitrogen gas flow. While the ideal (332) surface should show 1.2 nm broad terraces separated by monoatomic steps we found steps which were 2 to 5 nm high and terraces between 10 and 50 nm, as shown in a typical example in Fig. 7.



## Fig. 7



To overcome this facetting we tried another approach: after annealing we cooled the crystal in pure nitrogen in an electrochemical cell [4]. Then electrolyte  $(10^{-4} \text{ M HClO}_4, 10^{-4} \text{ M KI}, 10^{-2} \text{ M})$  NaClO<sub>4</sub>) was supplied and the potential was scanned between 0.02 and 0.9 V RHE to adsorb iodine on the surface. At 0.5 V the crystal was removed and rinsed with ultrapure water. By that way formation of large corrugations was avoided and the surface appeared rather flat, with a slightly corrugated row structure which resembles much more to what we would expect for the (332) face (Fig. 8). Distance of adjacent rows is 2-3 nm, which possibly indicates a  $(2 \times 1)$  reconstruction of the iodine covered Pt(332).



## Fig. 8

Topographic image of Pt(332) in air. Facetting is prevented by changing preparation procedure (details see text; the scan direction was not identical to that of Fig. 7). Scan area  $50 \times 50$  nm, scanning speed 100 nm/s

Trying the same preparation method on the Pt(110) single crystal gave the same results as shown in Figs. 5 and 6.

# **Adlattice Structures**

The atomic structure of the adsorbed iodine atoms was resolved in situ in the constant hight mode at increased scanning speed and decreased tunnel resistance (as compared to Figs. 3 and 4). The structure found in the case of the Pt(111) electrode at open circuit potential of 0.9 V is shown in Fig. 9. At this potential, a  $(3 \times 3)$ -I adlattice is expected from ex-situ LEED-experiments [12]. Our experimental lattice constants of  $a = 0.83 \pm 0.02$  nm and  $\alpha = 57^{\circ} \pm 3^{\circ}$  are close to the theoretical ones for the (3 × 3) lattice (a = 0.83 nm,  $\alpha = 60^{\circ}$ ). This structure is identical to one of the three (3 × 3)-I lattices previously imaged by STM in air [15].



#### Fig. 9

Current image (constant height mode) of Pt(111)-( $3 \times 3$ )-I, measured in situ in  $10^{-4}$  M KI,  $10^{-2}$  M NaClO<sub>4</sub>,  $10^{-4}$  M HClO<sub>4</sub> at open circuit potential of 0.9 V RHE, tunneling voltage -3 mV, scan area  $5.7 \times 5.7$  nm, scanning speed 780 nm/s





Current image (constant height mode) of Pt(100)-( $\sqrt{2} \times 5\sqrt{2}$ )-R 45°-I, measured in situ in 10<sup>-4</sup> M KI, 10<sup>-2</sup> M NaClO<sub>4</sub>, 10<sup>-4</sup> M HClO<sub>4</sub> at 0.75 V RHE, tunneling voltage -3 mV, scan area 6×6 nm, scanning speed 400 nm/s

We recently reported STM results on the iodine adlattice structure on Pt(100) in air [20]. Again the same structure  $((\sqrt{2} \times 5\sqrt{2})R45^{\circ})$  is found in electrolyte under potential control (0.75 V RHE) as shown in Fig. 10. Rows of iodine atoms run along the (001) direction. In the corresponding model, the iodine atoms in one of three rows are positioned in four fold hollow sites and therefore invisible in the STM-image. The two other rows are offset from on top positions by (1/6, 1/6) lattice constants of the substrate lattice. The analysis of a topographic image taken in air showed, that the experimental difference in height between these two different iodine atoms corresponds well with that determined theoretically from a simple ball model (approx. 0.7 A vs. 0.6 A theoretically) [21].

## Discussion

The above images show that the preparation of the low index faces (111) and (100) of Pt-single crystals using the

"iodine procedure" yields well defined, smooth surfaces, on which the atomic structure of the adsorbed iodine atoms can be resolved.

However, such a treatment causes facetting on the (332) face, which can be regarded as a (111) surface with monoatomic steps every 6 atoms. The predominance of multiatomic steps on the (111) oriented crystal is due to the same facetting. For clean Pt-surfaces with an orientation vicinal to the (111) plane, a surface structure with monoatomic steps is most stable [24]. The facetting therefore is induced by the adsorbed iodine. A similar, adsorbate induced facetting has been observed before for oxygen adsorbed on stepped Pt surfaces and other adsorption systems [24,25].

Facetting also occurs to some degree on the (110) face. The surface can be best described as  $(1 \times n)$  reconstructed, with n = 2 corresponding to the missing row structure. Higher values of *n* correspond to deeper valleys. This surface thus resembles the case of Au(110) [26] and the clean Pt(110) [22], for which also local  $(1 \times 3)$  reconstructions were observed. However, facetting seems to occur to a higher degree on the iodine covered Pt(110) surface, whereas on the adsorbate-free surface the local  $(1 \times 3)$  reconstruction only occurs between otherwise smooth terraces. It is noteworthy, that similar to the sulfur coated In(110) [27], the iodine covered Pt(110) surface is reconstructed at all, since many electronegative adsorbates remove clean surface reconstructions [25,27].

The clean Pt(100) surface is known to be reconstructed. This reconstruction is lifted by the adsorption of many species, whereby the excess Pt-atoms of the hexagonal surface layer are forced upward into a next layer and from islands, as shown by STM [28,29]. Annealing the Pt(100) crystal in the presence of iodine vapour also yields a surface without reconstruction [2]. In this case, one expects the direct formation of the unreconstructed, iodine covered surface without islands.

Our STM data show indeed, that such islands are absent on the iodine covered Pt(100). However, several deepenings surrounded by monoatomic steps are present on this surface. These are probably due to an incomplete coalescence of islands formed when during cooling of the crystal iodine starts beeing adsorbed.

The structures of the iodine adlattices are the same in air and in electrolyte. Our results not only confirm those of Schardt et al. for the (111) faces [10,15] but also the adlattice model structure for the (100) surface, which was obtained according to ex-situ (LEED) experiments [2].

Two points deserve a special attention:

1. For both the  $(111)(3 \times 3)$  adlattice and the  $(100)(\sqrt{2} \times 5\sqrt{2})$  adlattice the absolute position of the iodine atoms as suggested by the STM images is different from the model structures based on LEED results [2,12], although the adlattice itself is identical: Whereas, e.g., in the model structure for the  $(100)(\sqrt{2} \times 5\sqrt{2})$  adlattice 1/3 of the iodine atoms are positioned on top of a substrate Pt-atom, our STM results suggest that one third of the iodine atoms is in fourfold hallow sites (and therefore

invisible) and the other two third are only nearly on top [20]. This discrepancy, however, is not astonishing, since the model structures were only based on the diffraction pattern and not on intensity analysis. It should be stressed that for the  $(111)(3 \times 3)$  lattice an image was observed by Schardt et al. [15] (and reproduced by us) in which the atom position is identical to that in the model structures was recently observed [30] confirms that they are not due to electronic or tip effects. Recently, we have also found a  $(100)(1/2 \times 51/2)$  adlattice with the atom positions identical to the model based on LEED results [31].

2. The fact that the iodine adlattice on the (111) and (100) faces are identical in situ and in air justifies the ex situ experiments on one hand. But it also shows us, that the interactions of the adsorbate layer with the water are comparatively small. This is already suggested by the observed hydrophobicity of adsorbed iodine [12] and confirms that adsorbed iodine atoms are discharged. It remains to be shown that the same is true for other adsorbed anions.

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## References

- [1] J. Clavilier, R. Faure, G. Guinet, and R. Durand, J. Electroanal. Chem. 107, 205 (1980).
- [2] A. Wieckowski, S. D. Rosasco, B. C. Schardt, J. C. Stickney, and A. T. Hubbard, Inorg. Chem. 23, 565 (1984).
- [3] D. Zurawski, L. Rice, M. Hourani, and A. Wieckowski, J. Electroanal. Chem. 230, 221 (1987).
- [4] D. Armand and J. Clavilier, J. Electroanal. Chem. 270, 331 (1989).
- [5] D. M. Kolb, Ber. Bunsenges. Phys. Chem. 92, 1175 (1988).
- [6] H. D. Abruna (ed.), Electrochemical Interfaces, VCH, New York 1991.
- [7] J. Clavilier, R. Parsons, R. Durand, C. Lamy, and J. M. Leger, J. Electroanal. Chem. 124, 321 (1981).
- [8] T. Hartung, U. Schmiemann, I. Kamphausen, and H. Baltruschat, Anal. Chem. 63, 44 (1991).
- [9] O. M. Magnussen, J. Hotlos, R. J. Nichols, D. M. Kolb, and R. J. Behm, Phys. Rev. Lett. 64, 2929 (1990).
- [10] S.-L. Yau, C. M. Vitus, and B. C. Schardt, J. Am. Chem. Soc. 112, 3677 (1990).
- [11] S.-L. Yau, X. Gao, S.-C. Chang, B. C. Schardt, and M. J. Weaver, J. Am. Chem. Soc. 113, 6049 (1991).
- [12] F. Lu, G. M. Salaita, H. Baltruschat, and A. T. Hubbard, J. Electroanal. Chem. 222, 305 (1987).
- [13] M. Hourani and A. Wieckowski, J. Electroanal. Chem. 227, 259 (1987).
- [14] M. Wasberg, L. Palaikis, S. Wallen, M. Kamrath, and A. Wieckowski, J. Electroanal. Chem. 256, 51 (1988).
- [15] B. C. Schardt, S. L. Yau, and F. Rinaldi, Science 243, 981 (1989).
- [16] K. Besocke, Surf. Sci. 181, 145 (1987).
- [17] T. Michely, K. H. Besocke, and M. Teske, J. Microsc. 152, 77 (1988).
- [18] J. Giner, J. Electrochem. Soc. 111, 376 (1964), cited after C. H. Hamann and W. Vielstich, Elektrochemie II, p. 143, Weinheim 1981.
- [19] R. M. Penner, M. J. Heben, and N. S. Lewis, Anal. Chem. 61, 1630 (1989).

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- [20] R. Vogel and H. Baltruschat, Surface Sci. Lett. 259, L739 (1991).
- [21] P. Feng, W. Moritz, and D. Wolff, Phys. Rev. B 38, 7275 (1988).
- [22] T. Gritsch, D. Coulmann, R. J. Behm, and G. Ertl, Surf. Sci. 257, 297 (1991).
- [23] R. Vogel, PhD Thesis, University of Witten/Herdecke, FRG, 1991.
- [24] G. A. Somorjai, Chemistry in Two Dimensions, p. 166, Cornell University Press, Ithaca, London 1981.
- [25] G. A. Somorjai and M. A. van Hove, Progress in Surf. Sci. 30, 201 (1989).
- [26] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, Surf. Sci. 131, L 379 (1983).
- [27] C.-M. Chan and M. A. van Hove, Surf. Sci. 193, 303 (1987).
- [28] W. Hösler, E. Ritter, and R. J. Behm, Ber. Bunsenges. Phys. Chem. 90, 205 (1986).
- [29] E. Ritter, R. J. Behm, G. Pötschke, and J. Wintterlin, Surf. Sci. 181, 403 (1987).
- [30] S.-C. Chang, S. L. Yau, B. C. Schardt, and M. J. Weaver, J. Phys. Chem. 95, 4787 (1991).
- [31] R. Vogel and H. Baltruschat, J. Ultramicroscopy, accepted.
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