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LIST OF SYMBOLS

- activity referenced to the bulk-phase equlibrium avalue
- Α reaction in reduction reaction
- C D concentration, mol/cm³
- diffusivity, cm²/s
- \overline{f} **F** F/RT, mol/V-eq
- Faraday's constant, 96,485 C/eq
- ĥ interelectrode gap in flow cell, cm
- i current density normal to electrode, A/cm² number of electrons transferred, eq/mol
- $n \\ P$
- product in reduction reaction
- R T universal gas constant, 8.314 J/mol-K
- absolute temperature, K
- $\stackrel{-}{<} v_x > V$ average fluid velocity, cm/s
- electrode voltage, V
- $x \\ X$ distance along electrode, cm
- mole fraction in deposit
- \boldsymbol{y} distance normal to electrode, cm

Greek

- cathodic transfer coefficient α
- anodic transfer coefficient ß
- $\delta_{\rm c}$ mass transfer boundary layer thickness, cm
- overpotential, V η
- φ electrical potential, V

Subscripts

- limiting current density at zero surface concen-L
- tration
- k species k
- exchange current density tot
- total current

Superscripts

- reactant Α
- b bulk solution
- equilibrium value o P
- product
- s value at the electrode surface

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In Situ STM Studies of Lead Electrodeposition on **Graphite Substrate**

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ABSTRACT

Scanning tunneling microscopy (STM) was applied in solution to study the lead electrodeposition on single-crystal graphite electrode. The amount of deposited lead was varied from a few to a hundred monolayers. The atomic lattice of electrodeposited lead was observed and compared with that observed in air. The planes [111] and [100] of deposited lead crystallites were detected. The process of anodic dissolution of Pb deposit was studied by *in situ* STM also. During this process the changes of surface roughness were observed.

Scanning tunneling microscopy (STM) has already become an important tool in surface science. Efforts have been made to apply this technique to electrochemistry since 1986 (1-6).

STM can image real space and give structural, electronic, and chemical properties of the solid-liquid interface on an atomic scale. Atomic resolution has been obtained in

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UHV and air on different surfaces [metals and semiconductors (4)].

Similar resolution has been attained at the electrode/ electrolyte interface for highly oriented pyrolitic graphite (HOPG) electrodes (3). Structural features on the nanometer scale in the electrochemical environment have been found for single-crystal electrodes (7, 8) and polycrystalline materials (9, 10). Recently, Wiechers et al. reported the observation of atomic height steps on Au in situ and the change of the STM picture upon chloride ions adsorption, but atomic-level crystalline lattice for metals in contact with electrolyte solution has not been reported at this time (11).

In this paper, we report $in \, situ$ observations of the atomic crystalline lattice of lead (12).

Experimental

In the present study, a Nanoscope 1, Digital Instruments, Inc., California, was used. The instrument features a single-tube piezoelectric scanner with vertical tunneling tip.

The tip was mounted in the holder placed on the piezoelectric crystal which was held in the microscope head. The microscope head was placed on three adjustable screws (Fig. 1). Two of them, hand driven, were coarse adjustment screws. The third one was driven by stepper motor to control the fine adjustment of distance between the STM tip and the electrode.

The STM apparatus was protected against acoustic, mechanical, and electromagnetic vibration by placing it in boxes made of aluminum, lead, and copper. All this was placed on a big cement block in a sand bed laid on the top of a table floating on air. An inflated rubber tire was placed (Fig. 1) between the sand bed and air table. The STM setup described allowed us to obtain high-resolution images which are shown for the HOPG substrate in Fig. 2a and b.

The electrochemical cell for the three-electrode circuit (the STM tip was the fourth grounded electrode) was made of Delrin. Its thickness was ca. 5 mm (Fig. 3).

The working electrode was made of a 5×5 mm HOPG crystal. Before each experiment, the electrode surface was renewed by peeling off the top layers of the crystal by means of adhesive tape.

The counterelectrode was made of a platinum wire (99.99%) surrounding the working electrode (Fig. 3). A calomel electrode was used for reference. (Potentials reported in this paper are recalculated to hydrogen scale.)

The electrochemical potential of working electrode was adjusted by variation of the potential difference between working and counterelectrode using a battery powered voltage source.

The STM tips for the study carried in air were made of tungsten wire (0.1 mm diam). They were sharpened by electrochemical etching in 1M KOH. The tips used in solution were purchased from Longreach Scientific Resources. They were made of platinum and covered with a glass layer up to the operational tip.

On the basis of an electrochemical study of the electrode at the end of which was the tip, *i.e.*, by determination of the



Fig. 1. Schematic representation of STM setup: 1. copper cover, 2. lead cover, 3. aluminum cover, 4. microscope head, 5. piezo crystal tube, 6. STM tip holder, 7. STM tip, 8. electrochemical cell, 9. coarse adjustment screws, 10. fine adjustment screw, 11. microscope base, 12. aluminum base, 13. step-motor, 14. leg of microscope, 15. lead base, 16. cement block, 17. sand bed, 18. air tube, 19. floated table, 20. air tube, and 21. floated table leg.



Fig. 2. STM image of HOPG in air: (a, top) top view with drawn-in unit cell and benzine ring, grid dimension 4×4 Å, (b, bottom) side view, grid dimension 3×3 Å, and in Z (vertical) direction 2.5Å. $V_{\text{bias}} = 30 \text{ mV}$, $i_{\text{set point}} = 1.5 \text{ nÅ}$.

charge for hydrogen or oxygen adsorption on platinum, the real surface area was found to be 10^{-4} cm². (Tunneling tip was far smaller of course.)

The clarity of the images was related to the magnitude of the Faradaic currents. Clear images were observed for electrochemical currents smaller than 10 pA, but even for $i_{\rm F}$ up to 100 pA, some surface features could be observed. The 10 pA currents were observed for about 20% of the glass-covered tips. The applied tunneling bias voltages (potential difference between tip and working electrode) were between -100 and +100 mV. The images were recorded in constant current mode, *i.e.*, the distance between the tip and sample was varied during tunneling. The studied set point currents were between 0.5 and 5 nA. The



Fig. 3. Schematic representation of electrochemical cell for STM apparatus.

best results were obtained for a bias voltage around -50 mV (sample negative) and set point current $\sim 2 \text{ nA}$. A 5441 storage oscilloscope, Tektronix, was used as a registration device.

The solutions used were 10^{-3} Pb(ClO₄)₂ and 10^{-2} NaClO₄ and were prepared from Millipore-Q water, not deaerated during experiment.

Lead deposition was carried under constant current or constant potential conditions, as indicated below for individual systems. The amount of deposited lead was varied from a single monolayer to a few hundred monolayers. The thickness of lead deposits was calculated on the basis of the charge under a peak for the anodic dissolution of lead (Fig. 4, dashed line). In Fig. 4, the *i*-E dependence for the HOPG electrode is shown (Fig. 4, solid line).

The presence of lead on the surface of the electrode after deposition was confirmed by ESCA-XPS studies (Fig. 5). XPS analysis was carried with a Kratos XSAM 800 spectrometer with Al K α x-ray source. The pressure in the analyzer chamber was 1×10^{-7} /torr. Initially, a survey scan was recorded to identify the elements present on the surface. Subsequently, pertinent levels were then recorded over a narrow energy range.

The original spectra of Pb 4f levels (Fig. 5a) were next deconvoluted (Fig. 5b). Deconvolution showed two pairs of Pb 4f peaks 139, 141 and 146 eV. The appearance at the peaks at 141 and 146 eV is due to lead in an oxide form, probably formed during transport of the samples after STM experiment to the XPS chamber in contact with air.

The deposition of Pb on graphite was carried out when the STM tip was placed in solution but in a nontunneling mode. After each experiment was carried out *in situ* the STM tip was again used for monitoring the HOPG lattice in air to check that no lead was deposited on it. None was observed, *i.e.*, the graphite lattice was visible. The reproducibility of the images of electrodeposited lead was about 5%. The dimensions reported in this paper are the average of measured values. The indicated errors are mean deviations from the average values.

Results

In Fig. 6a, the stepped surface of an HOPG electrode in solution is shown. The wide ~ 90 nm steps, 3 atoms in height, are well resolved. Generally, our graphite surfaces were flat over a few hundred nanometers and it was difficult to find a step. In Fig. 6b and c, high-resolution images of a HOPG sample *in situ* are shown. In Fig. 6b, a three-

-0.75 -0.75 10μA 10μA 10μA 1200μA

Fig. 4. The *i-E* dependence of HOPG electrode in (--) 10⁻² NaClO₄ and (---) 10⁻³ Pb(ClO₄)₂ + 10⁻² NaClO₄ solution. Sweep rate 100 mV s⁻¹.



Fig. 5. XPS spectrum of Pb-HOPG electrode: (a) Pb 4f level spectra, and (b) deconvolution of Pb 4f level spectra.

dimensional picture (tilted, *i.e.*, a side view) is shown. The measured corrugation (peak-to-valley distance) is about 1.0 ± 0.2 Å. In Fig. 6c, the top view of the same part of the graphite surface is shown. This exposure led to the measurement of interatomic distances listed in Table I.

In Fig. 7 an STM of lead islets on HOPG taken in air after galvanostatic deposition is shown. The deposited amount of Pb was equivalent to two monolayers. The Pb deposits are represented by white spots which are visible mainly in the upper half of the photograph. In the bottom part of the image the hexagonal crystallographic pattern of graphite is distinguishable. On the basis of this photo the coverage of the electrode by deposit can be estimated as ~ 0.3 .

In Fig. 8, an STM picture taken in solution shows the appearance of Pb deposited potentiostatically at -0.24V. The deposited amount corresponds to four monolayers. The visible ordered spherical domains have ~ 20 Å in base and are 2-3Å high.

Figure 9 shows the STM picture of an electrode surface after the galvanostatic deposition of about 100 monolayers



Fig. 6. STM images of HOPG electrode taken in solution: (a) tilt view of big scan, grid dimension $X \cdot Y \cdot Z = 348 \times 348 \times 10$ Å, (b) tilt view, grid dimension, $X \cdot Y \cdot Z = 6 \times 6 \times 5$ Å, and (c) top view, grid dimension, $X \cdot Y = 8 \times 8$ Å. $V_{\text{bias}} = -50 \text{ mV}$, $i_{\text{s}} = 1 \text{ nA}$.

Table I. The interatomic dimensions of studied surfaces^a

Fig. No.	$\operatorname{Bond}^{\mathfrak{b}}$	Environmental	Distance ^c
2a 6c 11a 11b 11c 11d 12	C—C C—C C—C Pb—Pb Pb—Pb Pb—Pb	$\begin{array}{l} Air \\ 10^{-2} \ NaClO_4 \\ Air \\ 10^{-3} \ Pb(ClO_4)_2 + 10^{-2} \ NaClO_4 \\ 10^{-3} \ Pb(ClO_4)_2 + 10^{-2} \ NaClO_4 \\ Air \\ Air \\ Air \end{array}$	$\begin{array}{c} 2.3 \pm 0.2 \\ 2.3 \pm 0.3 \\ 2.4 \pm 0.2 \\ 2.4 \pm 0.2 \\ 3.6 \pm 0.3 \\ 3.1 \pm 0.4 \\ 3.5 \pm 0.1 \end{array}$

^a Distances were measured on the basis of manufacturer STM calibration (X = 20 Å/V, Y = 18 Å/V, Z = 20 Å/V). The average values are given independently of the axis of image.

values are given independently of the axis of image. ^b C—C distance is the distance measured between two carbon atoms having neighbors directly below in the next lower layer.

° Pb—Pb distances are given without calibration on graphite.

of Pb. The sloping hill is about 100\AA height and the angles to the horizontal $\sim 100^\circ$. The Pb deposit was then partially anodically dissolved at about 0 V. The roughness after this procedure was found to be 10-15Å (Fig. 10).

The smoothing of the deposit surface during dissolution was utilized in an experiment in which the aim was to obtain an image of lead atoms in contact with solution. In Fig. 11a-d, four pictures taken in the same experiment are shown. At the beginning, the lattice of HOPG electrode in air was monitored (Fig. 11a). Then, the solution (10^{-3}) $Pb(ClO_4)_2 + 10^{-2} NaClO_4)$ was added and the image of an electrode under open-circuit conditions was taken (Fig. 11b). Thereafter, a thick layer of lead was potentiostatically deposited at -0.36V. Next, part of the Pb deposit was removed by electrochemical dissolution to electropolish the surface of the deposit. The final thickness of the Pb layer corresponded to 80 monolayers. The STM image for this electrode was taken at -0.2V and it is shown in Fig. 11c. The interatomic distances are listed in Table I. In the next step of the experiment, the solution was removed from the cell, the electrode carefully washed with water, and then dried. The STM image for Pb deposit in air is shown in Fig. 11d. In the last step the 10⁻² NaClO₄ solution was added and the Pb layer was oxidized to measure the amount of lead present on the surface. After removing the solution, it was washed and dried and an image of the electrode was registered. It was found to be the same as presented in Fig. 11a.

Figure 12 is an STM image of a Pb deposit taken 12h after the deposit was made. The new tip, a tungsten one, was used to obtain this image (for dimensions, see Table I).

Discussion

In applying *in situ* STM techniques, one must recall certain requirements of the technique. They are: (*i*) The dumping of as much acoustic, electromagnetic, and mechanical vibration as possible. (*ii*) Maintenance of a constant temperature because of the danger of thermal drift



Fig. 7. STM image detected in air of Pb islets over lattice of HOPG surface. Grid dimension, $X \cdot Y = 18 \times 18$ Å, $V_{\text{bras}} = -50$ mV, $i_s = 2$ nA.



Fig. 8. STM image of an electrode registered in solution after deposition of four monolayers of Pb. Grid dimension, $X \cdot Y \cdot Z =$ $12 \times 12 \times 5$ Å. $V_{\text{bias}} = -50$ mV, $i_s = 2$ nA.

effects. Thus, the average thermal expansion coefficient for different materials is of the order of 10^{-6} mK⁻¹ (13) so that thermal stability of the STM setup is one of the most important requirements. In our experiments we make an attempt to attain thermal stability of the system by placing a foam layer on a copper box (Fig. 1). (*iii*) Diminishing the faradaic current flowing through the STM tip, necessary to obtain a clear and stable STM image due to tunneling current and not influenced by an electrochemical faradaic one that could make carrying out an STM experiment impossible.

The vibrational protection described in the Experimental section gave stable systems. In Fig. 2a and b and 11a images of HOPG taken in air, and in Fig. 6 and 11b taken in solution, are shown. The observed interatomic and 1.4 \pm 0.2 between nonequivalent atoms (Fig. 2a, in benzine ring) and its corrugation (0.8-1.5Å dependent on bias voltage) fit the experimentally detected values obtained in vacuum (14-20).

The STM image in Fig. 7 shows lead islet deposits (white spots) overimposed on HOPG lattice. In this case Pb had been deposited in galvanostatic mode. A resolution of the Pb lattice deposit was not obtained, probably owing to the roughness of the deposit.

The growth of a Pb deposit under potentiostatic conditions is shown in Fig. 8. The photograph was taken during deposition. The height of the hillocks is around 2-3Å but the width is surprisingly large, 10-20Å.

We have observed the reflection of lattice angles on lead deposits *ca.* 100 monolayers thick (Fig. 9 and 10). The observed angles are 110° (Fig. 8) and 60° (Fig. 9). The hills in the Pb deposits shown in Fig. 9 and 10 are visible on the lead layer and not directly on the graphite surface because of the large amount of deposited lead.



Fig. 9. STM image (in solution) of thick Pb deposit. Grid dimension X \cdot Y \cdot Z = 19 \times 19 \times 90Å. V_{bias} = 32 mV, i_s = 2 nA.



Fig. 10. STM image (in solution) of thick Pb deposit after its partial dissolution. Grid dimension $X \cdot Y \cdot Z = 19 \times 19 \times 10$ Å. $V_{\text{bios}} = 32 \text{ mV}$, $i_s = 2 \text{ nA}$.

The polishing effect of dissolution can be seen by a comparison of the height of the Pb hills between images shown in Fig. 9 and 10. The height of the electropolished humps in Fig. 10 is ten times smaller than those before polishing. This electropolishing effect was used to prepare smooth surface of the Pb deposit in order to monitor lead atomic lattice. The photographs shown in Fig. 11a-d were taken under the same tunneling condition and with the same tip. It is clear that images in Fig. 11c and d differ from images shown in Fig. 11b and a taken before Pb deposition, respectively. The interatomic distances in Fig. 11c and d and in Fig. 11a and b, are 3.6Å and 3.1Å, and 2.4Å and 2.4Å, respectively.

The Pb-Pb distances cited in literature depend on the type of contact between lead atoms and vary from 3.0\AA (21), to 3.5\AA (13, 22), 3.6\AA (23), 3.8\AA (24), and 3.9\AA (24).

Images shown in Fig. 11c and d cannot represent information from a graphite lattice because the amount of deposited Pb was big enough to fully cover the HOPG substrate and its thickness is around 300Å; so the STM monitoring of a support, *i.e.*, graphite surface, is impossible. Correspondingly, the observed interatomic distances are bigger than those expected (and obtained here) for graphite (cf. Table I). One could argue that the presented photographs (Fig. 11c and d) are the images of the platinum tip. The interatomic distance for Pt-Pt is expected to be 2.75Å (13), but detected distances range between 3.1 and 3.7Å.

In Fig. 12 a further image of a Pb deposit is presented. In this case, the surface of the deposit was prepared as in an experiment leading to the images recorded and presented in Fig. 11a-d, but then the solution was removed and the electrode washed and dried. We allowed a time of 12h to ellapse. A new tungsten tip was applied to scan the surface. The measured interatomic distance is ± 3.6 Å. The angles measured between rows of atoms were 50° and 130°, in comparison with the expected angle for a hexagonal plane (111) of 60° and 120°. Again the W-W interatomic distance was only 2.74Å (13).

In the present discussion, atomic distances and angles have been considered. Such a use neglects questions of the crystal plane being observed. The deposits made are undoubtedly polycrystalline, i.e., different crystalline faces are exposed. The ratio between different faces depends on the condition of electrodeposition, because the rate of growth of specific faces differs one from the other (25). According to this mechanism, the surface of the deposit should be bounded with edge boundaries. In fact, in some cases the surface of the deposit would be expected to be bounded by grain boundary faces parallel to the substrate (26). Additionally, it seems that the application of the electropolishing procedure increases the degree of crystallographically uniform surface, probably because of the differing stability of the various crystal faces. These reasons, together with the fact that the scanning area is small,



Fig. 11. The images of graphite surface detected in (a, top left) air and (b, top right) solution; the images of lead deposited on graphite surface detected in (c, bottom left) solution and (d, bottom right) air. Grid dimension $X \cdot Y = 9 \times 9$ Å. $V_{\text{bias}} = -30$ mV, $i_s = 1.5$ nA.



Fig. 12. The image of lead deposited on HOPG registered in air. Grid dimension $X \cdot Y = 4 \times 4$ Å.

 72×72 Å (Fig. 11c and d) or 32×32 Å (Fig. 12), explains the fact that we observed the well-ordered lead lattice instead of random-oriented Pb atoms.

Thus, for the image presented in Fig. 11c, an angle of $90^{\circ} \pm 5^{\circ}$ and distances 3.6 ± 0.3 are detected and this would mean that the observed plane is [100] which is in agreement with the view that preferred orientation axes for the lead electrodeposits is [100] (27, 28).

The image shown in Fig. 12 has the appearance of a hexagonal [111] face which supports Finch and Layton's view (29) on the lateral-type growth of fcc metals under low current density conditions (deposition at -0.26V, *i.e.*, small overvoltage). There is a clear difference between the images presented in Fig. 11c and Fig. 12. The first one was taken directly after preparation of the surface, while the second one was taken after 10h. Hence, a time-dependent surface reconstruction may be responsible for this difference or it may be because a different crystallite was monitored.

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