JOURNAL OF THE ELECTROCHEMICAL SOCIETY

ACCELERATED

BRIEF COMMUNICATIONS

AUGUST
1989

Atomic Resolution of Carbon and Lead Atoms from Measurements Made in Solution

M. Szklarczyk,[1] O. Velev, and J. O'M. Bockris*

Surface Electrochemistry Laboratory, Texas A&M University, College Station, Texas 77843-3255

STM is rapidly evolving into a powerful technique for a wide application to study electrochemical systems [1-6]. The aim of this communication is to show that atomic resolution in electrolyte solution for different materials than HOPG is possible. In this note the results on in situ STM studies of lead deposits on graphite substrate are shown. The solution was $10^{-3}Pb(ClO_4)_2 + 10^{-2}NaClO_4$.

In the present study the STM Nanoscope 1, Digital Instrument, Inc., and 5441 Storage Oscilloscope, Tektronix, as a registration device were used. The STM apparatus was protected against acoustic, mechanical and electromagnetic vibration by placing it on the top of an air table in boxes made of copper, lead and aluminum. The images were recorded in constant current mode for ex situ and in situ experiments. The set point currents for experiments carried in air and solution were 2.9 nA and 2.0 nA, respectively. The Faradic current between STM tip and substrate was kept below 0.05nA. The bias potential was -50mV (sample negative).

In Fig. 1 a high resolution image for HOPG in air is presented. Solution was added to the cell and the image for HOPG in solution shown on Fig. 1b was registered. Thereafter a thick layer of lead was deposited at -0.6V vs SCE. Then, part of the Pb deposit was removed by oxidation to smooth the surface of the deposit. The final thickness of the Pb layer corresponded to ca 80 monolayers. The registered image for this electrode is shown in Fig. 2a. Then the solution was removed from the cell and the electrode was washed and dried. The image for HOPG - Pb in air is shown on Fig. 2b. In the next step the Pb layer was electrochemically removed of HOPG surface, than electrode was washed and dried again. The surface image after this procedure was the same as presented in Fig. 1a. All presented here images were registered with the same STM tip.

The experimental values of the nearest neighbor distances are shown in the Table. There is good agreement between the STM obtained values in air and those reported in literature [6]. The different distances for lead atoms in solution and in air were detected (cf. Table). It is possible that such differences are caused by different state of oxidation of lead in solutions and in air.

The images registered for the substrates placed in the solution are not so clear (more "noisy") as those observed in air. One reason for this may be the difference in capacity of the solution and the air layers between the substrate and STM tip (higher capacity, higher capability of assorbance of noises). Thus for organic solvents, a higher STM resolution then that in aqueous solutions should be obtainable.

The authors are grateful for discussion with Dr. B. Womack of Oak Ridge National Laboratory, Dr. A. Wieckowski of the University of Illinois, and Dr. B. Schardt of Purdue University. They acknowledge a sharing of costs of the equipment with the Center for Electrochemical systems and Hydrogen Studies. They are also grateful for support to the Texas A&M University in the form of an enhancement of research grant, and to the Welch Foundation for the support of this work in its preliminary stages.

References

1. B. Drake, R. Sonnefeld, J. Schneir, P. K. Hansma, Surf. Sci., 18, 92 (1987).
2. F. R. F. Fan, A. J. Bard, Anal. Chem., 60, 751 (1988).
3. O. Lev, F. R. Fan, A. J. Bard, J. Electrochem. Soc., 135, 783 (1988).
4. C. L. Perdriel, E. Custidiano, A. J. Arvia, 246, 165 (1988).
5. R. Lustenberger, H. Rohrer, R. Christoph, H. Siegenthaler, J. Electronal. Chem., 243, 225 (1988).
6. J. Wiechers, T. Twomey, D. M. Kolb, R. J. Behm, J. Electroanal. Chem., 248, 451 (1988).
7. P. Batra, N. Garcia, H. Rohrese, H. Saleminik, E. Staly, S. Cyraci, Surf. Sci., 181, 126 (1987).
8. CRC Handbook of Chemistry and Physics, 1979-1980 edition. R. C. Weast, ed., CRC Press, Inc., Boca Raton, Florida.

---

[1] On leave from Department of Chemistry, Warsaw University, 02-089 Warsaw, Poland.

*Electrochemical Society Active Member.

SUMMARY OF NEAREST NEIGHBOR DISTANCES (Å) DETECTED BY STM.

	AIR	SOLN	LITERATURE (X-RAY)	
Graphite	2.5 ± 0.2	2.5 ± 0.3	2.5[1]	[7]
Lead	2.9 ± 0.3	3.9 ± 0.3	3.5	[8]

Manuscript received Nov. 28, 1989.
Texas A&M University assisted in meeting the publication costs of this article.

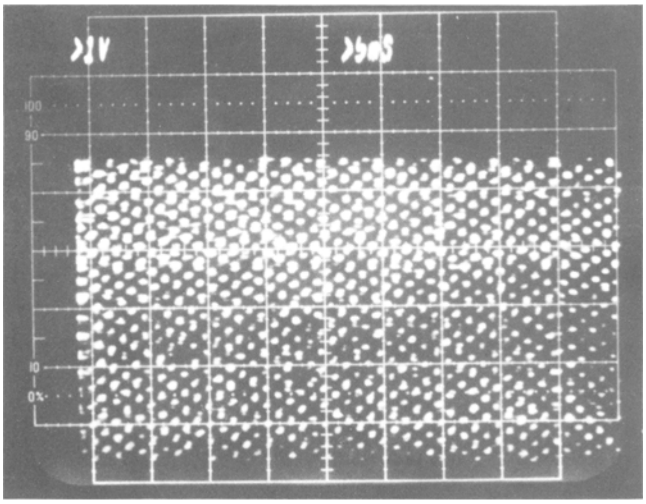

Fig. 1a The image of graphite surface detected in air. The grid dimension is 9Å x 9Å (the same for all figures).

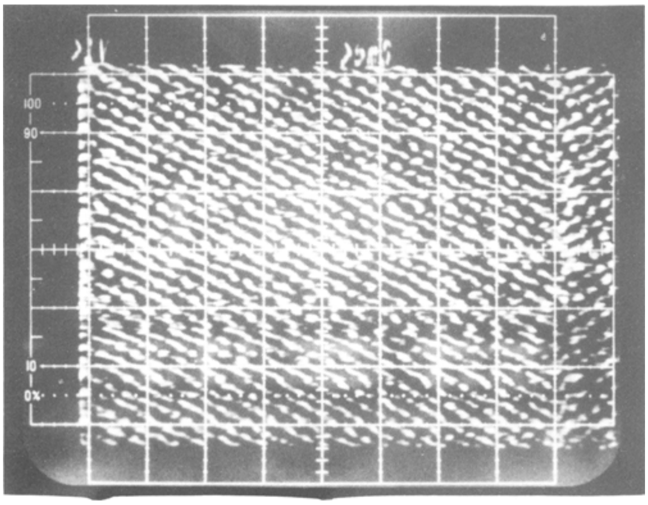

Fig. 1b The image of graphite surface detected in solution.

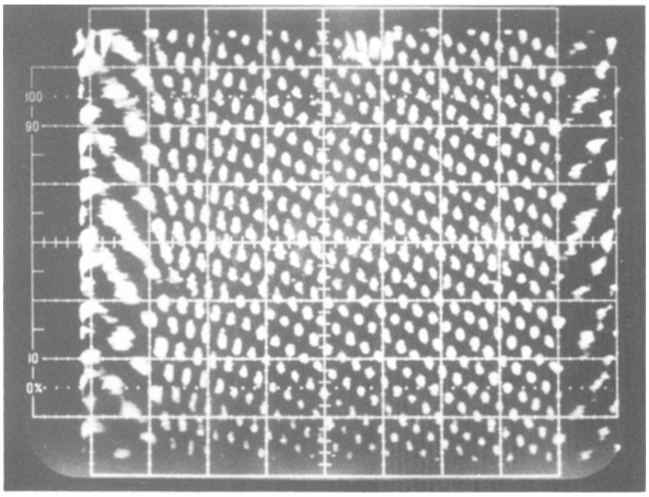

Fig. 2a The image of Pb massive deposit detected in solution.

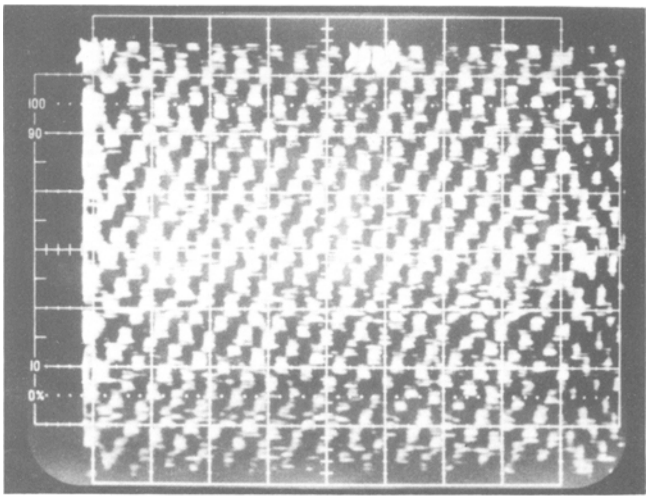

Fig. 2b The image of Pb massive deposit detected in air.

---

[1] The STM image of graphite is known to be centered hexagon with 2.5Å periodicity arising from atoms having no neighbors directly below in the next lower layer.