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In Situ AFM Study of Interlayer Spacing during Anion Intercalation into HOPG in Aqueous Electrolyte

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In the context of ion transfer batteries, highly oriented pyrolytic graphite (HOPG) was studied as a model in aqueous electrolytes to elucidate the mechanism of electrochemical intercalation into graphite. The local and time-dependent dimensional changes of the host material occurring during the electrochemical intercalation processes were investigated on the nanometer scale. Atomic force microscopy (AFM), combined with cyclic voltammetry, was used as an in situ analytical tool during the intercalation of perchlorate and hydrogen sulfate ions into and their expulsion from the HOPG electrodes. For the first time, a reproducible, quantitative estimate of the interlayer spacing in HOPG with intercalated perchlorate and hydrogen sulfate ions could be obtained by in situ AFM measurements. The experimental values are in agreement with theoretical expectations, only for relatively low stacks of graphene layers. After formation of stage IV, HOPG expansion upon intercalation typically amounts to 32% when tens of layers are involved but to only 14% when thousands of layers are involved. Blister formation and more dramatic changes in morphology were observed, depending on the kind of electrolyte used, at higher levels of anion intercalation.

1. Introduction

Graphite is an excellent choice for the negative electrode of "rocking-chair" batteries[1] due to its high charge density and superior cycling behavior. However, despite its rapid diffusion and commercialization in modern batteries, several problems remain unresolved. One major lacuna concerns the dimensional changes occurring during electrochemical processes. A knowledge of these changes is fundamental for an understanding of the electrochemical intercalation/insertion mechanism and for the evaluation of potential practical applications.

The macroscopic changes occurring in the mechanical properties of graphite during insertion have been investigated for many years[2]. While the ion exchange between an electrode and the bathing electrolyte may be monitored by techniques such as probe beam deflection (PBD) or electrochemical quartz crystal microbalance (EQCM),[3] an in situ observation of dimensional changes of the electrodes is difficult. Neutron,[4] X-ray[5] diffraction, and dilatometry[6] techniques can provide average information about the overall results of the intercalation processes, but are completely useless on a local microscopic scale.

Scanning probe microscopy[7] techniques can be used to investigate the surface of graphite electrodes under potential control and to probe thickness changes or local electronic properties, even on a nanometer scale.[8,9] Recently, Li^+ intercalation has been observed in situ by scanning tunneling microscopy (STM)[10] and atomic force microscopy (AFM),[11] which proved to be powerful techniques in the context of battery research.

Several authors have already studied the electrochemical behavior of graphite in aqueous electrolytes.[12] Beck et al.[13] showed that the perchlorate ion is one of the best intercalating species at relatively low acid concentrations ($2-4$ M $HClO_4$), while hydrogen sulfate ions can intercalate efficiently only at higher molarities (10 M H_2SO_4).[14] The relationship between intercalation processes and side reactions such as oxidation was investigated by Alsmeyer and McCreery.[15] Their Raman evidence for graphite lattice damage occurring as a consequence of anion intercalation suggests that the graphite intercalation compounds (GIC) initially formed will subsequently oxidize carbon to form graphite oxides. The observation of surface blister formation on graphite in concentrated acid electrolytes at high potentials by AFM[16] and STM[17] was taken as further evidence for a correlation between initial intercalation and subsequent oxidation. At low electrode potentials, no damage of the graphite surface was observed.[18] The latter

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(1) Vincent, C.; Scrosati, B. *Modern Batteries: An Introduction to Electrochemical Power Sources*, 2nd ed.; Arnold: London, 1997.

(2) Ebert, L. B. *Annu. Rev. Mater. Sci.* **1976**, *6*, 181.

(3) Miras, M. C.; Barbero, C.; Kötz, R.; Haas, O.; Schmidt, V. M. *J. Electroanal. Chem.* **1992**, *338*, 279.

(4) Zhou, P.; Fischer, J. E. *Phys. Rev.* **1996**, *B53*, 12643.

(5) Carr, K. E. *Carbon* **1970**, *8*, 155.

(6) Biberacher, W.; Lerf, A.; Besenhard, J. O.; Mohwald, H.; Butz, T. *Mater. Res. Bull.* **1982**, *17*, 1385.

(7) Binning, G.; Quate, C. F.; Gerber, C. *Phys. Rev. Lett.* **1986**, *56*, 930.

(8) Siegenthaler, H. In *Scanning Tunneling Microscopy II*; Wiesendanger, R., Guentherodt, H. J. Eds.; Springer-Verlag: Berlin, 1993.

(9) Gewirth, A. A.; Siegenthaler, H. *Nanoscale Probe of the Solid/Liquid Inferface*; Nato ASI Series E: Applied Science, Vol. 288; Kluwer Academic Publishers: Dordrecht, 1995.

(10) Inaba, M.; Siroma, Z.; Funabiki, A.; Ogumi, Z. *Langmuir* **1996**, *12*, 1535.

(11) Chu, A. C.; Josefowicz, J. Y.; Farrington, G. C. *J. Electrochem. Soc.* **1997**, *144*, 4161.

(12) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; John Wiley & Sons: New York, 1988.

(13) Beck, F.; Junge, H.; Krohn, H. *Electrochim. Acta* **1981**, *26*, 799.

(14) Kang, F.; Zhang, T.-Y.; Leng, Y. *J. Phys. Chem. Solids* **1996**, *57*, 883.

(15) Alsmeyer, D. C.; McCreery, R. L. *Anal. Chem.* **1992**, *64*, 1528.

(16) Goss, C. A.; Brumfield, J. C.; Irene, E. A.; Murray, R. W. *Anal. Chem.* **1993**, *65*, 1378.

(17) Zhang, B. L.; Chi, Q.; Dong, S.; Wang, E. *Electrochim. Acta* **1995**, *40*, 733.

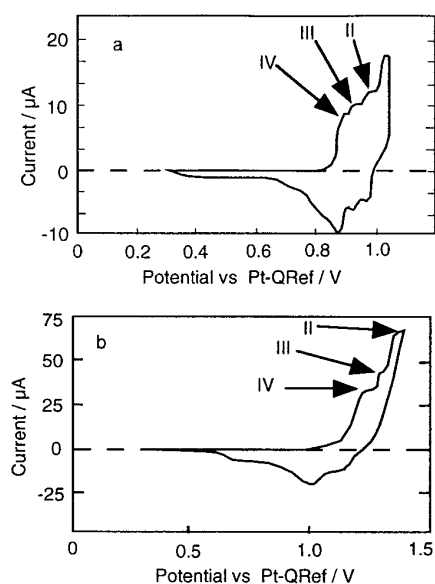(18) Zhang, J.; Wang, E. *J. Electroanal. Chem.* **1995**, *399*, 83.

Figure 1. Cyclic voltammograms (second cycle) recorded at HOPG in 2 M $HClO_4$ (a) and in 1 M H_2SO_4 (b). Scan rate: 25 mV/s. According to the literature,[13] peak positions on the potential scale are typical for stages IV, III, and II.

observation suggests that the contribution of side reactions can be minimized by selecting the right combination of acid concentration and electrochemical potential.

Table 1. Charges in the Voltammograms of Figure 1[a]

CV	ion	Q_A (mC/cm²)	Q_C (mC/cm²)	Q_C/Q_A
1a	perchlorate	7.15	5.51	0.8
1b	sulfate	43.7	13.39	0.3

[a] Q_A, anodic charge; Q_C, cathodic charge. All values are normalized with respect to the HOPG area.

In the present communication, the system of highly oriented pyrolytic graphite (HOPG) in perchloric acid is examined as a model in order to elucidate the mechanism of electrochemical anion intercalation in graphite. Perchlorate ions were selected because of their excellent intercalating property at relatively low acid concentrations. Further experiments were conducted with sulfuric acid in order to see whether the type of electrolyte has any influence on the intercalation mechanism.

More specifically, we performed a local and time-dependent investigation of dimensional changes of the host material on the nanometer scale during the electrochemical intercalation processes. AFM, combined with cyclic voltammetry, was used as an in situ analytical tool during intercalation and deintercalation of perchlorate and hydrogen sulfate ions in HOPG.

2. Experimental Details

The AFM investigations were performed with an Autoprobe CP (Park Scientific Instruments, Sunnyvale, CA) atomic force microscope, which was calibrated according to the procedure
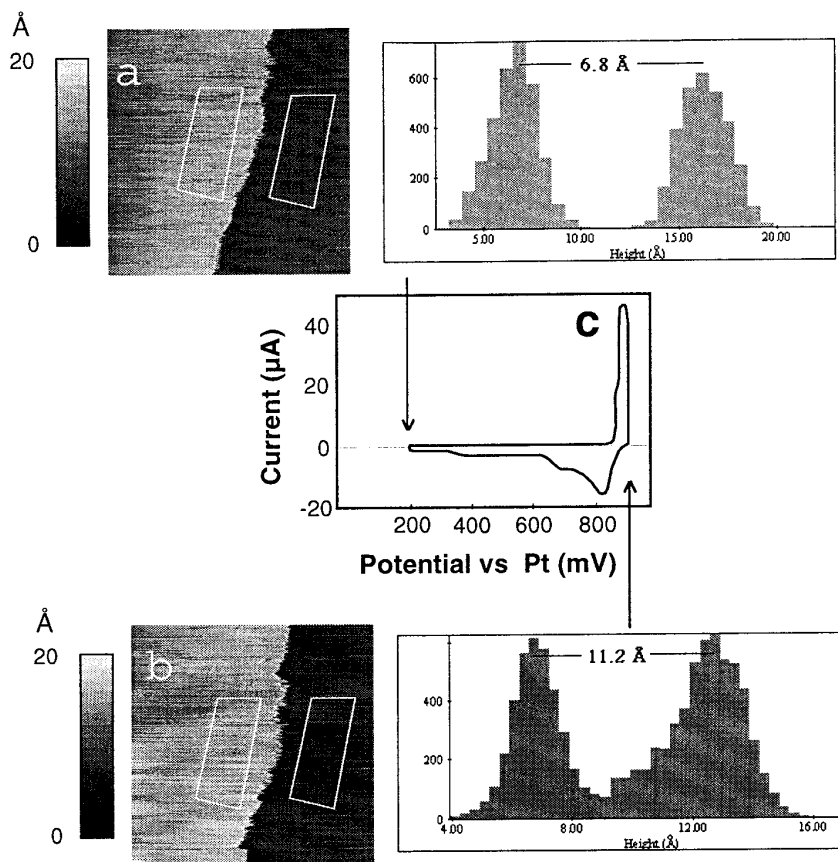

Figure 2. AFM images of a given HOPG bilayer in 2 M $HClO_4$ at different potentials. (a) HOPG before intercalation (+200 mV). (b) Sample was imaged after waiting for 4 min to intercalate the anions (+920 mV). (c) Corresponding cyclic voltammogram acquired at a scan rate of 25 mV/s. For each AFM image, the acquisition time was about 4 min. Height distributions pertaining to the regions marked are shown on the right.
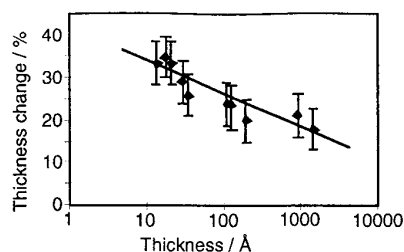
Figure 3. Increase in interlayer distance between graphene layers (percentage value) after formation of stage IV in 2M HClO$_4$ as a function of the thickness of the step. Potential was scanned from the open circuit value to 920 mV (scan rate 25 mV/s) and held for 4 min.

developed by Staub and co-workers.[19] This instrument was equipped with an electrochemical cell and an EG&G Versastat 270 potentiostat/galvanostat for in situ measurements. A platinum quasi reference electrode (Pt-QRef)[20] showing a drift of less than 10 mV/h was used in the AFM electrochemical cell. All potentials are quoted against the Pt-QRef, which in turn was +700 ± 20 mV versus the saturated calomel electrode (SCE).

As a working electrode, we used a HOPG ZYH-type crystal (Advanced Ceramics Corporation, Lakewood, OH) with a Mosaic spread of 3.5°, according to X-ray diffraction (XRD) measurements. All the HOPG electrodes were prepared in rectangular shape, with a length and width of 3−4 mm and a thickness of 1 mm. They were freshly cleaved with adhesive tape prior to each experiment. The total side faces of the sample were painted with an insulating varnish in order to prevent exposure of the HOPG edge planes to the electrolyte.

The electrolytes were 2 M HClO$_4$ and 1 M H$_2$SO$_4$ solutions prepared by mixing ultrapure water with 60% concentrated HClO$_4$ or 98% concentrated H$_2$SO$_4$. The starting acids were purchased from Fluka.

Cyclic voltammograms of the HOPG electrodes were acquired with the AFM electrochemical cell at a scan rate of 25 mV/s. The AFM images were acquired with a 100 μm scanner in the contact mode at constant force. The typical scan rate was 1 Hz, and silicon cantilevers from Park Scientific Instruments (Ultralevers) were used.

The height of an HOPG step was obtained by calculating the difference between the mean values of height measured in two marked areas on the top and bottom layer of the step. This procedure was essential in order to average out the noise contributions and the statistical fluctuations in height due to the local aspect of the process.

All theoretical values for the dimensions of stacks sequences of HOPG layers were calculated by considering an interlayer spacing of 3.35 Å for unfilled gaps[21] (nominal spacing for the ABAB structure of HOPG), 7.95 Å for a gap filled with perchlorate ions, and 7.98 Å for a gap filled with hydrogen sulfate ions.[22]

In the line measurement mode,[23] the AFM tip was always scanning across the same line (scan speed 0.5 Hz, pixel resolution 256 256), while the potential of the sample was cycled between 550 mV and 950 mV for 7 round trips, with a scan rate of 25 mV/s. An equilibration time of 8 s before scanning the potential and a waiting period of 20 s at both scan inversion points were also introduced. The resulting total acquisition time was 8 min 32 s. The changes in thickness and bias of the sample were recorded simultaneously.

3. Results and Discussion

3.1. Cyclic Voltammetry. Perchlorate ion intercalation

(19) Staub, R.; Alliata, D.; Nicolini, C. *Rev. Sci. Instrum.* **1995**, *66*, 2513.

(20) Brett, C. M. A.; Brett, A. M. O. *Electrochemistry Principles, Methods and Applications*; Oxford University Press: Oxford, 1993; p 138.

(21) Pierson, H. O. *Handbook of Carbon, Graphite, Diamond and Fullerenes*; Noyes Publications: Park Ridge, 1993.

(22) Aronson, S.; Lemont, S.; Weiner, J. *Inorg. Chem.* **1971**, *10*, 1296.

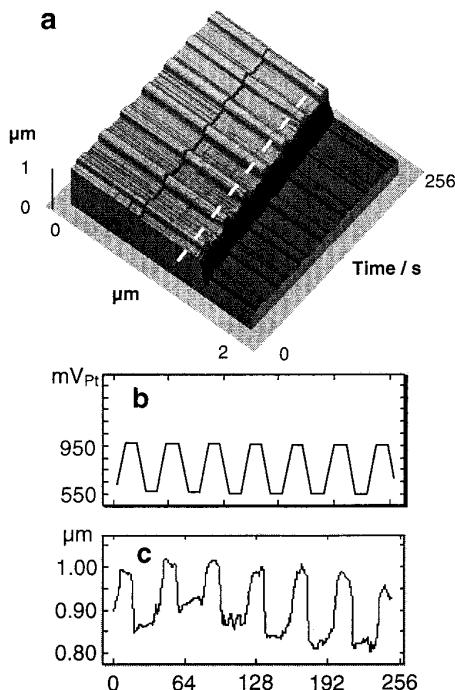(23) Häring, P.; Kötz, R.; Repphun, G.; Siegenthaler, H. *Appl. Phys. A* **1998**, *66*, S481.

Figure 4. AFM image of an HOPG step region in 2 M HClO$_4$ recorded with the probe scanning a line while cycling the potential of the sample between +550 mV and +950 mV: (a) 3-dimensional view; (b) potential transients; (c) height profile corresponding to the dashed line in the 3-dimensional view.

into the HOPG basal planes was induced under well-controlled conditions in 2 M HClO$_4$. As shown in Figure 1a, different stages of graphite intercalation compounds (GIC) can easily be distinguished in the cyclic voltammograms. Over a potential range of only about 200 mV, up to three different stages of intercalation of anions and associated solvent or acid molecules into the graphite lattice are visible in the form of anodic peaks in the positive scan, which reappear as cathodic peaks in the negative scan.

The main reaction involved is

$$[C_x] + [A^-] + y(\text{solv}) = [C_x^+ A^- (\text{solv})_y] + e^- \quad (1)$$
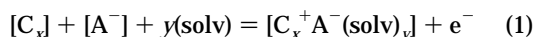
Below a certain potential, reaction 1 is nearly reversible for a 2 M HClO$_4$ solution. For potentials too far on the anodic side, the reversibility of reaction 1 decreases, and other reactions (graphite oxide formation, carbon dioxide formation, water electrolysis) can take place.[24]

A typical voltammogram for HOPG in 1 M H$_2$SO$_4$ is shown in Figure 1b. Again, reaction 1 is responsible for the appearance of anodic peaks and cathodic counterpeaks. However, in this case side reactions are much more important, which can be seen by comparing the oxidative (Q_A) and reductive (Q_C) charges associated with the corresponding voltammograms in Figure 1. In Table 1, these values of charge are compared in order to estimate the degree of reversibility of the intercalation process. The values of Q_A were calculated by integrating the CVs over the potential range between 0.85 V and the potential of anodic scan reversal. The values of Q_C represent the total cathodic charge above 0.3 V. Whereas for intercalation of perchlorate ions, the charge efficiency is still relatively high even for stage II formation ($Q_C/Q_A = 0.8$),

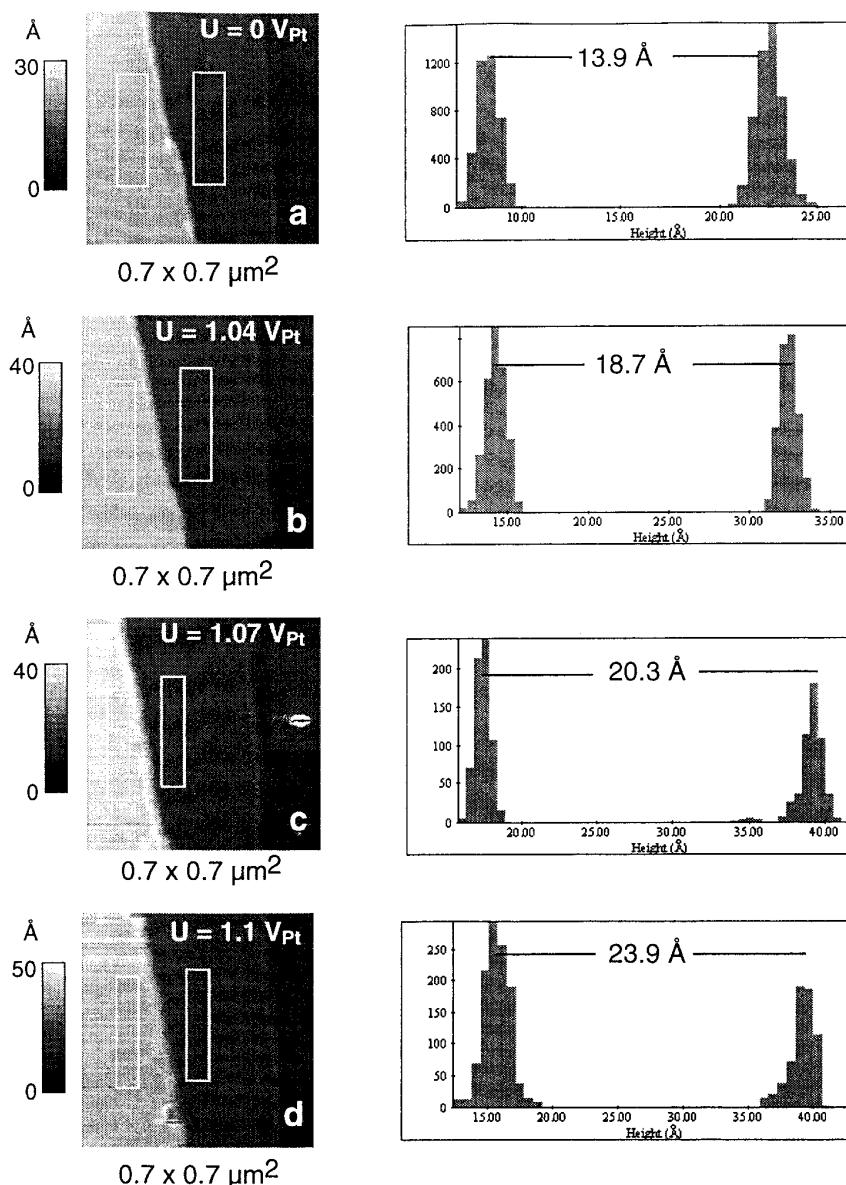(24) Beck, F.; Krohn, H. *Synth. Met.* **1983**, *7*, 193.

Figure 5. Sequence of AFM images of a given HOPG four-layer step in 2 M HClO$_4$ at different potentials: (a) before intercalation; (b) stage IV; (c) stage III; (d) stage II.
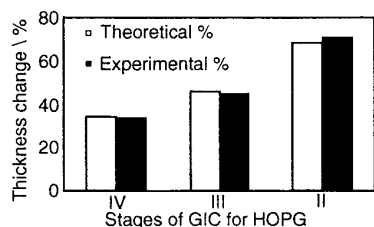

Figure 6. Histogram showing the percentage interlayer distance change for different stages: comparison of experimental and theoretical values.

in the case of hydrogen sulfate ions, the anodic charge is much higher than the cathodic one ($Q_C/Q_A = 0.3$) and, as a consequence, the reversibility of the intercalation process is reduced.

3.2. Perchlorate Ions: Stage IV. The process of stage IV formation and dissolution was investigated on HOPG

in 2 M HClO$_4$. Dimensional changes of the HOPG steps were studied over a range of heights between 6.7 Å, corresponding to a bilayer of HOPG planes, and a micrometer, corresponding to thousands of HOPG planes. A bilayer step on an HOPG crystal was imaged under potential control, before and after formation of stage IV. Before intercalation (+200 mV), the height of the step was 6.8 Å, as shown in Figure 2a. After formation of stage IV (+900 mV), the height of the step had increased to 11.3 Å (Figure 2b). Since the distance between carbon layers upon incorporation of perchlorate ion is 7.95 Å (see Experimental section), this increase in step height is exactly what we expect and confirms our preliminary results concerning the same system.[25] Then, the potential was returned to the original value and maintained for 10

(25) Alliata, D.; Häring, P.; Kötz, R.; Haas, O.; Siegenthaler, H. 5th International Conference on Nanometer-Scale Science and Technology (NANO 5), Birmingham, UK, 1998; Abstr PSPTu54.
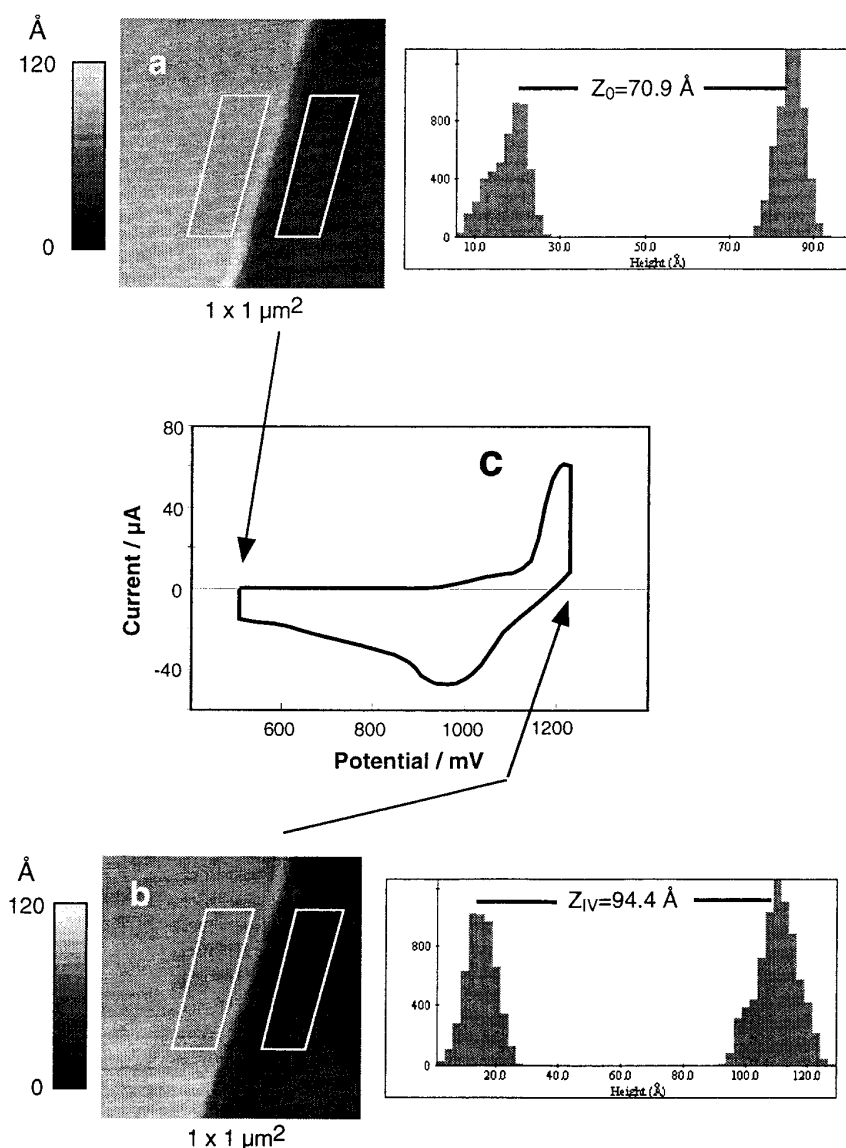
Figure 7. AFM images of a given HOPG multilayer in 1 M H_2SO_4 at different potentials: (a) HOPG before intercalation (+500 mV); (b) after waiting for 4 min to intercalate the anions (+1250 mV); (c) corresponding cyclic voltammogram acquired at a scan rate of 25 mV/s. For each AFM image the acquisition time was about 4 min. Height distributions pertaining to the regions marked are shown on the right.

min. As a result, the height of the bilayer decreased to 6.7 Å (image not shown), which is very close to the initial value. When applying this method to other steps, sometimes the time dependence of the two processes (intercalation and deintercalation) appears to be different. This aspect was described in a separate publication.[26]

The same experimental approach was repeated at steps with different heights, that is, different numbers of carbon layers. According to the dimensions cited above for the perchlorate ion, we always expected an increase in height of about 34% for every sequence of four—or multiple of four—graphene layers (stage IV). However, this expectation was only confirmed for steps smaller than 50 Å. As shown in the diagram plotted in Figure 3, the percentage

change of the interlayer distance decreases with an increasing number of graphene layers involved in the intercalation process.

This result is not completely surprising. As already discussed by Winter and co-workers when studying graphite as a negative electrode for lithium-ion cells,[27] the intercalation of species into graphite generally requires considerable energy, since the gaps between the graphene layers held together by van der Waals forces must be expanded. The expansion energy depends on the mechanical flexibility of graphene layers deformed by the intercalation process, and the energy increases with the number of adjacent graphene layers present on both sides of a particular gap.[28] Therefore, intercalation generally begins close to the surface, in the gap adjacent to the top basal planes. Then, the intercalation progresses toward internal layer gaps.

(26) Alliata, D.; Häring, P.; Haas, O.; Kötz, R.; Siegenthaler, H. *Electrochem. Commun.* **1999**, *1*, 5.

(27) Winter, M.; Novak, P.; Monnier, A. *J. Electrochem. Soc.* **1998**, *145*, 428.

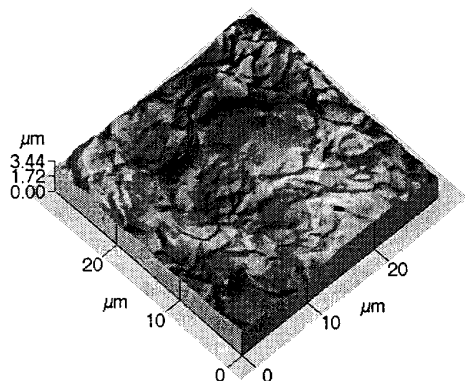(28) Hooley, J. G. *Mater. Sci. Eng.* **1977**, *31*, 17.

Figure 8. Effect of oxidation on the morphology of a fresh HOPG crystal in 1 M H_2SO_4 after two potential cycles between 0 and 1.25 V.

A second additional explanation for this result resides in the fact that the probability of defects and vacancies increases with the number of graphene layers, that is, with the thickness of the step. The presence of these defects can prevent the perchlorate ions from intercalating, since the adjacent layers are pinned together and difficult to move with respect to one another. As a consequence, the usable capacity for insertion is reduced, which was actually shown in recent studies of the properties of synthetic and natural graphite.[29]

The movement of graphene layers, for instance from AB- to AA-stacking, can also influence the interlayer distance. However, this is mainly important for stage I compounds, as suggested by Moret,[30] and it should be less effective for stage IV compounds, which are investigated here.

Our AFM measurements of relative expansion are in apparent discrepancy with previous dilatometry measurements of crystals in highly concentrated sulfuric acid,[31] which had shown a relative thickness variation of 34% during stage IV formation for 0.01-mm-thick HOPG. This may be due to a different quality of the HOPG samples. In fact, the importance of a highly graphitized structure for the effective formation of GIC[32] is well-known.

In an effort to study the reproducibility of the intercalation process, we imaged a step on an HOPG crystal with the AFM working in the xzt mode. In this case, the AFM tip was forced to cross a step of 146 nm, corresponding to 438 HOPG layers, at the same fixed line position while the electrode potential was scanned between 550 mV and 950 mV (see Experimental section for more details). The resulting image is shown in Figure 4a. The thickness variation is clearly reflected in the alternating peaks and valleys, which correlate with the intercalation and deintercalation of perchlorate ions in HOPG, respectively.

The thickness change observed at the bottom of the step in Figure 4 is a consequence of the intercalation of perchlorate ions into a second step outside the field of view.

The correlation between thickness variation and HOPG potential is more clearly visible when we examine the
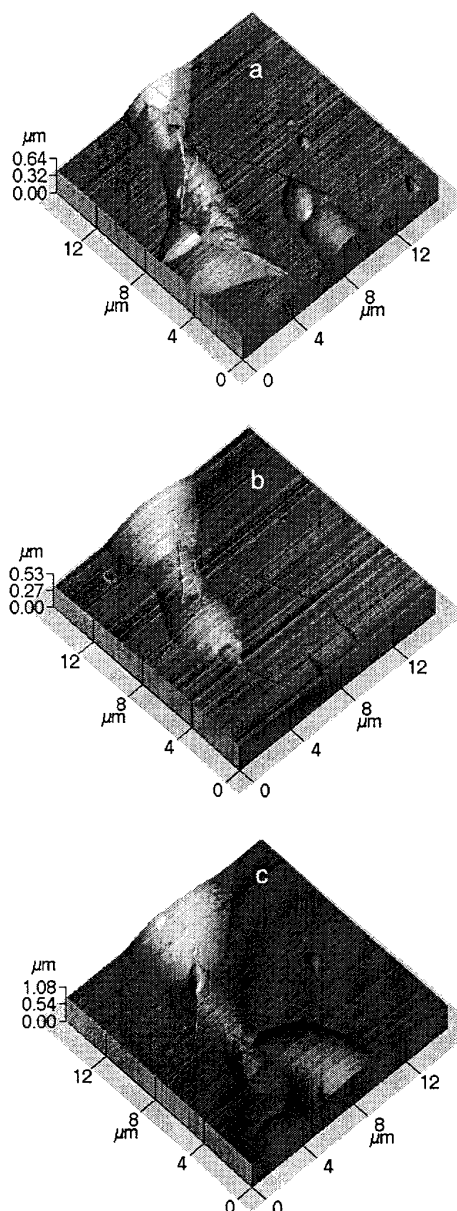
(29) Shi, H.; Barker, J.; Saïdi, M. Y.; Koksbang, R. *J. Electrochem. Soc.* **1996**, *143*, 3466.
(30) Moret, R. *Intercalation of Layered Materials*; NATO ASI Series; Dresselhaus, M. S., Ed.; Plenum Press: New York, 1986, B148, p 185.
(31) Besenhard, J. O.; Wudy, E.; Mohwald, H.; Nickl, J. J.; Biberacher, W.; Foag, W. *Synth. Met.* **1983**, *7*, 185.
(32) Rhodes, E., Proceedings of the Fifth International Power Symposium, Brighton, 1966; In Power Sources 1966; Collins, D. A., Ed.; Pergamon Press: London, 1966. Hathcock, K. W.; Brumfield, J. C.; Goss, C. A.; Irene, E. A.; Murray, R. W. *Anal. Chem.* **1995**, *67*, 2201.

Figure 9. Blister formation under potential control on a HOPG crystal in 2 M $HClO_4$: (a) 0 V; (b) 0.95 V; (c) 0 V.

height profile plotted across a line parallel to the HOPG step (Figure 4c) together with the potential transients (Figure 4b). The contribution of the above-mentioned second step was subtracted in order not to overestimate the change in thickness. The change is about 26 nm, corresponding to a percentage variation of 18.7%. This result proves that the interlayer distance of the graphene layers varies reversibly between the original value typical for a sequence of unfilled gaps and the "intercalated" value for a sequence of gaps filled with perchlorate ions. In this case, since the number of graphene layers involved in the process is high, the expansion measured by AFM (18.7%) is lower than that theoretically expected for stage IV (34%).

3.3. Perchlorate Ions: Stages IV, III, and II. After having focused our attention on the stage IV formation and disappearance, we studied the lower stages (stage III and stage II). To do this, a step of four graphene layers on an HOPG crystal was imaged at different potentials.

First, it was imaged at 0 V. The corresponding AFM picture and height distribution is shown in Figure 5a. Then, it was imaged at 1.04 V (Figure 5b), 1.07 V (Figure 5c), and 1.1 V (Figure 5d), corresponding to the potentials for the formation of stages IV, III, and II, respectively.

After the formation of each stage, the potential was returned to 0 V in order to dissolve the stage, and then the step was imaged again to test the reversibility of the process. The histogram plotted in Figure 6 summarizes the percentage changes in interlayer spacing for the formation and dissolution of every stage with reference to the expected theoretical values.

Unfortunately, it was not possible to study the formation of stage I, because the potential required was so high that side reactions took place, and as a result, the surface of the HOPG crystal was irreversibly damaged (blister formation, etching of the step).

3.4. Hydrogen Sulfate Ions: Stage IV. To study the influence of the type of electrolyte on the intercalation process, a second system was investigated by in situ AFM. A freshly cleaved HOPG electrode was exposed to a 1M H_2SO_4 solution. In Figure 7, a step of 21 layers is imaged before and after intercalation of sulfate ions. The corresponding histograms show the increase in step height of 33.1%, which is very close to the expected expansion of the interlayer spacing after formation of stage IV. However, after a few (2 to 3) cycles, the process cannot be reproduced anymore. For instance, Figure 8 shows how the surface of an HOPG crystal was damaged after two cycles in potential between 0 and 1.25 V.

Compared to the system of HOPG in perchloric acid that was investigated earlier, HOPG in sulfuric acid is much more sensitive to irreversible modifications of its surface due to the presence of side reactions (graphite oxide formation, carbon dioxide formation, water electrolysis), which are running in parallel with the intercalation (see Table 1 for the comparison of the charge efficiencies). This is mainly due to the fact that the potential we have to apply to induce sulfate-ion intercalation is higher than the potential required to intercalate perchlorate ions. As a result, the surface of HOPG is destroyed much more easily in sulfuric than in perchloric acid.

3.5. Blister Formation. Blister formation was occasionally noticed on basal planes after the intercalation of perchlorate ions. We observed blisters becoming larger or smaller, depending on the applied potential (Figure 9). The three AFM images of Figure 9 show the dynamics of formation and partial disappearance of a group of blisters as a result of several cycles of potential between 0 and 0.95 V. In the first image (Figure 9a), two groups of blisters are clearly visible at 0 V. When the potential is moved to +0.95 V (Figure 9b), the smaller group of blisters is no longer present, and part of the larger blister has disappeared. When the potential was moved back to 0 V (Figure 9c), the blister group reappeared and some blisters merged.

This blister formation is similar to that observed by Murray and co-workers[33] on an HOPG surface in less concentrated electrolytes and is probably associated with the same mechanism of formation. Murray et al. proposed a model in which blister formation reflects the intercalation of electrolyte and water into HOPG followed by subsurface gas evolution (electrolysis).

4. Conclusions

For the first time, a reproducible, quantitative estimate of the interlayer spacing of graphene layers could be obtained by in situ AFM measurements for the $HClO_4-$GIC (stage IV, III, and II) and H_2SO_4-GIC (stage IV) formation in HOPG. In perchloric acid, the experimental values are in agreement with the theoretical expectation only for small stacks of graphene layers. For a larger number of layers, the percentage of interlayer distance change decreases. Furthermore, blister formation in perchloric acid was observed as a function of the applied potential. Finally, as a consequence of the much lower charge efficiency, only the stage IV formation could be evaluated in H_2SO_4. The corresponding experimental values for the change of interlayer spacing are again in agreement with the theoretical expectation. Compared to the results for the stage IV formation in perchloric acid, dramatic changes of the surface morphology are observed already after 2−3 intercalation cycles in sulfuric acid. The effect of the intercalation process on other properties of the graphite surface (friction and work function) is currently being studied in our laboratory.

(33) Hathcock, K. W.; Brumfield, J. C.; Goss, C. A.; Irene, E. A.; Murray, R. W. *Anal. Chem.* **1995**, *67*, 2201.