ELSEVIER

Journal of Power Sources 69 (1997) 97-102

JOURNAL OF POWER SOURCES

Investigation of graphite composite anode surfaces by atomic force microscopy and related techniques

Karen Akemi Hirasawa [1], Keiko Nishioka, Tomohiro Sato, Shoji Yamaguchi *, Shoichiro Mori

Mitsubishi Chemical Corporation, Tsukuba Research Centre 8-3-1 Chuo, Ami, Inashiki, Ibaraki 300-03, Japan

Received 20 December 1996; accepted 1 February 1997

Abstract

The surface of a synthetic graphite (KS-44) and polyvinylidene difluoride binder (PVDF) anode for lithium-ion secondary batteries is imaged using atomic force microscopy (AFM) and several related scanning probe microscope (SPM) instruments including: dynamic force microscopy (DFM), friction force microscopy (FFM), laterally-modulated friction force microscopy (LM-FFM), visco-elasticity atomic force microscopy (VE-AFM), and AFM/simultaneous current measurement mode (SCM). DFM is found to be an exceptional mode for topographic imaging while FFM results in the clearest contrast distinction between PVDF binder and KS-44 graphite regions. © 1997 Elsevier Science S.A.

Keywords: Scanning probe microscopy; Friction force microscopy; Graphite; Carbon; Lithium-ion batteries; Polyvinyl difluorofluoride

1. Introduction

High safety, capacity and stability during cycling have resulted in an increased interest in 'rocking-chair' lithium-ion secondary batteries. In order to improve the performance of these batteries, the main focus has been on the development of anode materials. Several carbonaceous materials, including cokes and graphite, have been proposed as anode materials to be used in combination with an $LiCoO_2$ cathode and an organic electrolyte; of these, graphite is the most promising candidate for achieving a volumetric battery capacity of more than 300 Wh l^{-1}. As a result of increased analysis of anode materials, acquiring new methods of anode characterization has become a growing industrial priority. The scanning probe microscope (SPM) [1] has been found to be an effective tool for surface analysis at both the microscale and the nanoscale levels. Using the atomic force microscopy (AFM) — a scanning probe microscope (SPM) instrument that detects van der Waals interaction between the cantilever (sensor probe) and sample — it is possible to image both the electrical conductors and the insulators. Consequently, AFM has a great advantage over the first SPM reported in 1982, namely, scanning tunneling microscopy (STM) which detects a tunneling current between a sharp metal tip and the sample and is only able to image conductive materials. The ability to image electrical insulators is especially important when imaging actual composite electrodes used in battery cells that contain non-conductive binder material for mechanical support.

In addition to topographic mapping, measurement of other properties that include friction, visco-elasticity, and electrical conductivity is also possible. This is of particular interest in the study of graphite composite electrode samples since the binder and graphite regions can be distinguished.

There are several instruments in the SPM family that are useful for imaging graphite anode samples. The dynamic force microscopy (DFM) or tapping mode AFM (TMAFM) that operates by vibrating the cantilever near its resonance frequency is an alternative to the AFM for topographic imaging. This mode causes less damage to soft samples since the sample surface is only touched periodically [2]. For binder and graphite distinction, the friction force microscopy (FFM) or lateral force microscopy (LFM), can be used to image frictional differences in a sample by detecting the lateral bending of the cantilever that is often the result of frictional properties [3]. Nevertheless, since large topographic changes may also affect the lateral movement of the cantilever, laterally modulated friction force microscopy (LM-FFM) may be used; through the lateral modulation of the sample, topographic effects contributing to the lateral motion of the cantilever are reduced [4]. Visco-elastic properties may also be used to distinguish between materials using the

---

* Corresponding author. Tel.: +81 (298) 88 24 98; Fax: + 81 (298) 87 33 08.

[1] On leave from Queen's University, Kingston, Ont. K7L3N6, Canada.

PII S0378-7753(97)02578-0

visco-elasticity atomic force microscopy (VE–AFM). By modulating either the sample or the cantilever (a technique also referred to as 'force modulation'), visco-elasticity data can be collected [5]. As well, conductivity differences within a sample can be detected by the AFM/simultaneous current measurement mode (SCM). In this mode, an applied voltage results in current flowing through the sample which is measured simultaneously along with AFM topography data using a gold-coated cantilever.

Recently, Inaba et al. [6] reported topographical changes in the basal plane of highly oriented pyrolytic graphite (HOPG) during polarization, observed by in situ electrochemical STM at potentials greater than 1.1 V. Although such model studies on HOPG are useful in understanding surface reactions in graphite anodes, it is also essential to study actual composite electrodes. This is now possible using AFM and related techniques. Furthermore, since electrochemical STM is restricted by a limit on the potential applied to the sample in the electrochemical cell, Inaba et al. [6] were prevented from reporting images taken at less than 1.1 V versus Li/Li^+. In order for lithium intercalation to occur, a large faradic current flow, corresponding to a potential near 0 V versus Li/Li^+, is required and this interferes with the STM tunneling current feedback. Since AFM imaging has no such limitations, it is considered to be an ideal instrument for in situ electrochemical studies with a large potential range. Initial AFM topographic work on graphite anodes provides a basis for in situ electrochemical AFM studies on both HOPG and composite electrodes presently in progress to further the understanding of dynamic electrochemical processes at the anode/organic-electrolyte interface.

In this study, the surface of a graphite anode for lithium-ion secondary batteries is imaged using the SPM instrument. Synthetic graphite (KS-44), and polyvinylidene difluoride (PVDF) are chosen as the respective graphite and binder materials since they have attained widespread use [7]. An HOPG/PVDF binder sample with known binder/graphite areas is used to model graphite/binder boundaries on the composite electrode surface. Using this sample, several different SPM modes are tested to provide a basis for composite electrode sample imaging. This preliminary topography and binder/graphite work is important in determining the ideal SPM modes for specific samples and provides valuable topography and binder distribution data.

2. Experimental

The anode was prepared by mixing a carbon slurry that contained a 2% solution of polyvinylidene difluoride (PVDF) binder (Kureha, KF-1000), dimethylacetamide, and KS-44 graphite powder (mean diameter 18 μm, Lonza, Japan). The slurry was spread on a sheet of copper foil (thickness 18 μm) by the 'doctor blade method' and dried in an oven at 80 °C for 15 min. This resulted in a final graphite powder content of 90% in the electrode film. Finally, the film was pressed to a thickness of approximately 40 μm to allow for SPM observation. To provide a reference sample with known binder and graphite regions, a 2% PVDF solution was dropped on the surface of a cleaved piece of HOPG (12 mm × 12 mm × 1 mm, Advanced Ceramics, STM-1 grade) and dried in an oven at 80 °C for 15 min.

A JEOL JSM-6300F SME was used. All SPM images were taken in air, using an SPI3700 SPM (Seiko Instruments), with 20 and 150 μm piezo-scanners (1.82 μm, 5.44 μm z-height allowances, respectively). For AFM, FFM, LM–FFM, and VE–AFM measurements, commercially available triangular Si_3N_4 cantilevers with pyramidal tips (200 μm length, 0.02 N/m force constant, Seiko Instruments SN-AF01) were used. Rectangular Si cantilevers (230 μm length, 16 N/m force constant, Seiko Instruments SI-DF20) were employed for DFM imaging, and rectangular gold-coated Si cantilevers (450 μm length, 0.13 N/m force constant, Seiko Instruments SI-AF01-A) were used for SCM imaging. Force reference values used during SPM imaging were within the range of 10^{-11} and 10^{-9} N.

3. Results and discussion

3.1. Topographic study using AFM and DFM

The AFM contact mode and DFM were compared for imaging the topography of the graphite anode surface. These techniques are widely recognized and the operation and theory of both the AFM and DFM are well documented in the literature [8,9]. In the AFM contact mode, the cantilever constantly contacts the sample throughout the scan duration. As a result, sample destruction and the removal of delicate surface features may occur. The DFM minimizes this surface destruction by utilizing a tapping mechanism in which the cantilever only periodically touches the sample surface. For topographical imaging of the graphite anode surface, the DFM resulted in clearer images with more visible surface detail that was perhaps damaged by the constant AFM cantilever contact. Another imaging problem, especially in large scans, was the large change in topography that was present even after pressing the graphite anode. Since DFM had a larger z-axis tolerance, topographical images with a large area (over 20 μm) were more easily obtained. A typical 150 μm DFM image of the graphite anode is shown in Fig. 1. Using AFM, a comparable image of this large scan area was significantly more difficult to achieve.

Although the topography of the graphite electrode was visible in SEM images, height, friction, conductivity, and visco-elasticity data were not available using SEM. Fig. 2 shows a typical SEM image with a magnification approximately equal to the 3 μm topography images generated with various SPM modes. The graphite electrode topography is very similar in the SEM and SPM images. Binder distinction is not possible, however, with SEM. Since the SPM instrument is able to collect absolute height information, surface

Fig. 1. Typical 150 μm × 150 μm image of KS-44/PVDF (90/10) graphite anode using DFM.

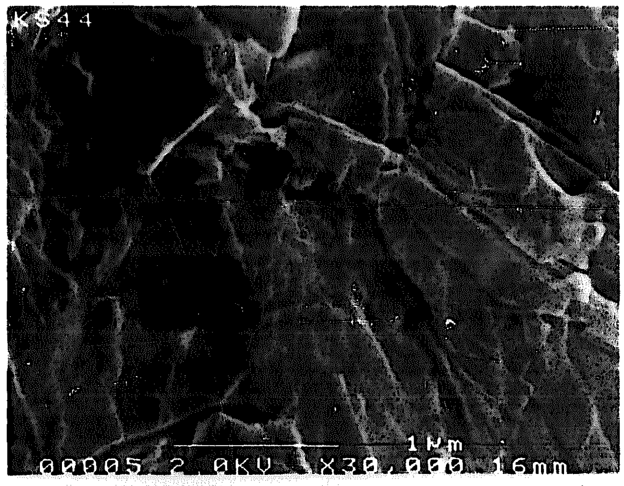

Fig. 2. Electron micrograph (×30 000 magnification) of KS-44/PVDF (90/10) graphite anode.

roughness and other quantitative data can also be measured. Thus, it is a more desirable instrument for topography analysis. The surface roughness parameter for this particular sample (shown in Fig. 1) is calculated to be 329.7 nm.

3.2. Binder and graphite distinction

The reference HOPG/PVDF sample was used to test the SPM modes which had the capability to differentiate between graphite and binder properties. Using this sample, it was possible to test contrast differences due to contrasting material properties and interpret subsequent images on composite graphite anode samples. For this purpose, images were taken at the binder and graphite boundary.

Several SPM modes (i.e., FFM, LM–FFM, VE–AFM and SCM) were used to image material properties in order to distinguish between the binder and graphite regions. In all cases, image contrast was visible between the binder and graphite areas on the reference sample. This warrants the use of these modes to distinguish binder and graphite areas in the composite graphite anode.

3.2.1. Friction force microscope

The friction force microscopy (FFM) detects the lateral bending of the cantilever, which is often the result of differences in frictional forces between the cantilever and the sample surface [3]. Since PVDF and graphite are expected to have significantly different frictional properties, FFM is predicted to be effective in distinguishing between the two. Indeed, images of the HOPG/PVDF reference sample show a clear distinction between the binder and graphite areas. Imaging of the graphite anode also reveal contrasting binder and graphite areas. Opposite FFM image contrast is obtained for rotation values of +90° and −90° because the direction of lateral cantilever twisting with respect to the scanning direction is altered. With a rotation value of +90° (Fig. 3),

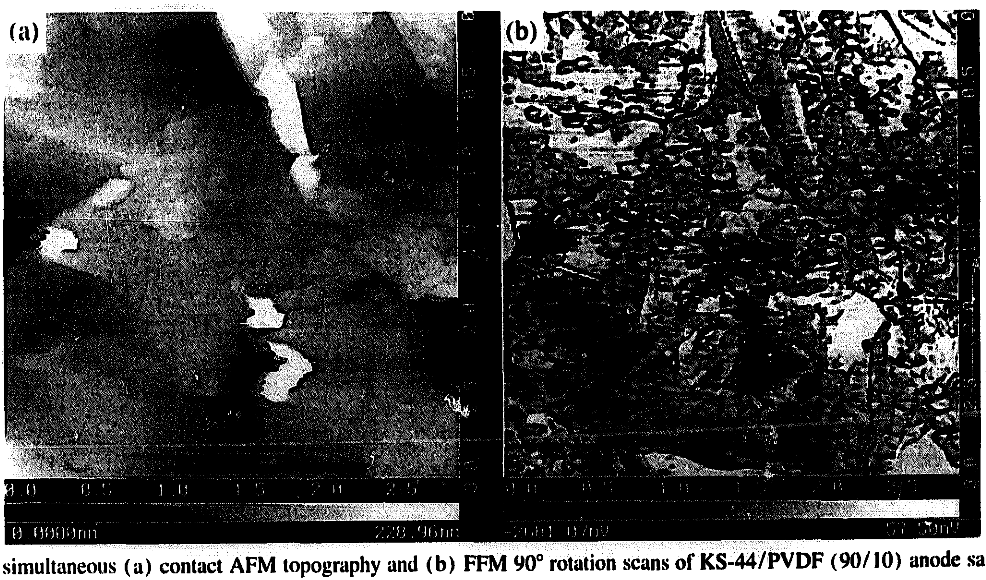

Fig. 3. 3 μm × 3 μm simultaneous (a) contact AFM topography and (b) FFM 90° rotation scans of KS-44/PVDF (90/10) anode sample. Darker areas in AFM scan correspond to lower areas. Darker areas in FFM scan correspond to higher friction (PVDF) regions.

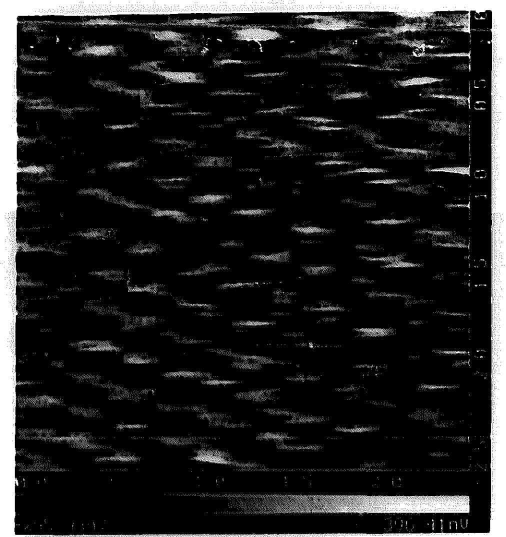

Fig. 4. 2.5 nm × 2.5 nm FFM atomic scan of uncovered graphite region in composite graphite anode sample showing an ordered graphite lattice structure.

darker areas correspond to binder regions while lighter areas correspond to bare graphite regions. With a rotation value of −90°, the opposite contrast occurs, i.e. darker areas correspond to graphite regions. To test further the FFM differentiation between the binder and graphite, atomic imaging was attempted on several regions. Ordered structures (Fig. 4), corresponding to bare graphite areas, are only visible in lighter contrast regions for the case of a +90° rotation. This confirms the contrast interpretation.

In addition to frictional differences, large topography changes may also result in the lateral bending of the cantilever. To reduce such unwanted topographical effects, the laterally modulated friction force microscope (LM–FFM) is an alternative [4]. Using this mode, differences in the binder and graphite regions are clearly visible in both the reference sample (HOPG/PVDF) and the graphite anode sample. Fig. 5 shows an LM–FFM scan taken in the same area as the FFM image in Fig. 3. Since frictional differences between the binder and graphite are likely to be very large, however, topographic influences are not a large problem. This is confirmed by the similarity of the images in Figs. 3 and 5.

3.2.2. *Visco-elasticity AFM (VE–AFM)*

The VE–AFM is able to distinguish between materials on the basis of the different visco-elastic properties of materials through cantilever modulation. Detailed explanations of this mode of observation are described in Ref. [5]. Using VE–AFM, the reference sample displays image contrast between the HOPG and binder covered areas. In the composite electrode sample (Fig. 6), lighter and darker contrast regions could also be identified, although the boundaries between these regions are not as sharply defined as in the FFM images. It is unknown whether this contrast is influenced by visco-elasticity differences between the binder and graphite or elastic deformation that results from the packing structure of the graphite powder and binder. Although VE–AFM is a promising technique for binder and graphite distinction, further work must be done before VE–AFM contrast can be effectively used to differentiate between binder and graphite areas.

3.2.3. *AFM/simultaneous current measurement mode (SCM)*

The SCM measures the flow of current through a sample resulting from an applied voltage, while simultaneously measuring AFM topographic data using a gold-coated cantilever. By imaging the HOPG/PVDF model sample, differences in electrical conductivity between the binder and graphite become apparent, with the binder area exhibiting far less electrical conductivity than the graphite area. For 3 μm scans, distinction between graphite and binder are apparent (Fig. 7), although boundaries between the two materials are again not as sharp as in the FFM images. Although acceptable images are obtained in smaller scans, in larger scans of over 10 μm, there is a strong correlation between the simultaneous AFM topography images and the SCM images. It is probable

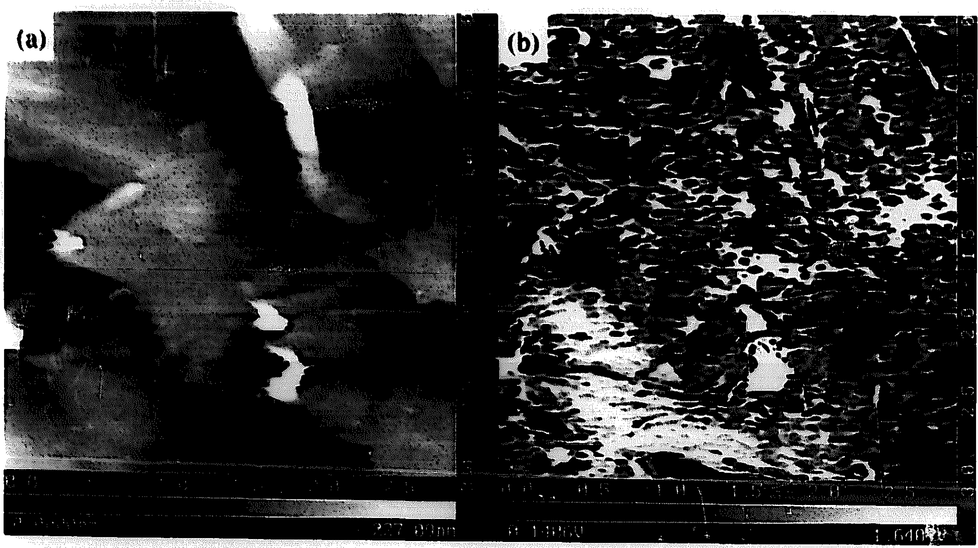

Fig. 5. 3 μm × 3 μm simultaneous (a) contact AFM topography and (b) LM–FFM scans of KS-44/PVDF (90/10) anode sample. Darker areas in AFM scan correspond to lower areas. Darker areas in LM–FFM scan correspond to lower friction (KS-44) regions.

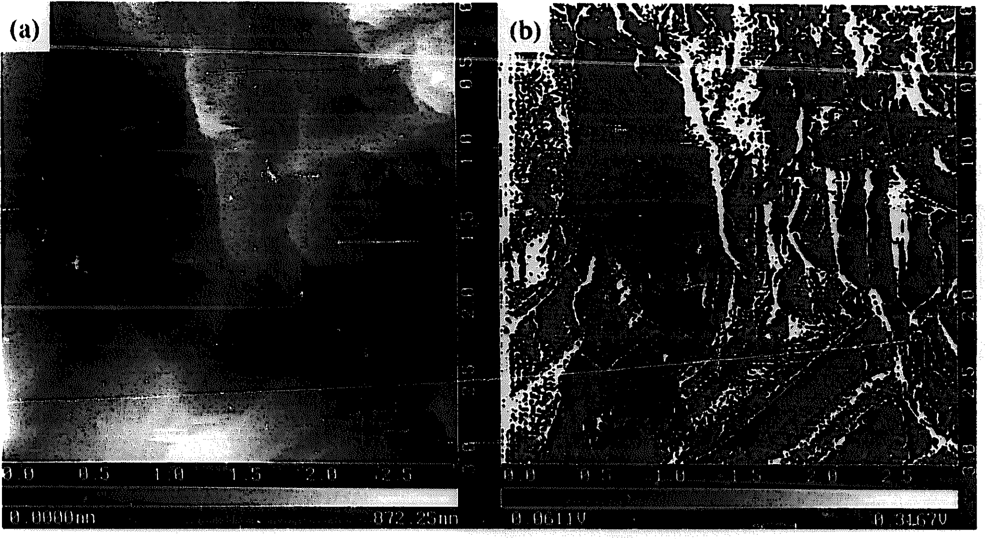

Fig. 6. 3 μm × 3 μm simultaneous (a) contact AFM topography and (b) VE–AFM scans of KS-44/PVDF (90/10) anode sample. Darker areas in AFM scan correspond to lower areas. Darker areas in VE–AFM scan correspond to KS-44 regions.

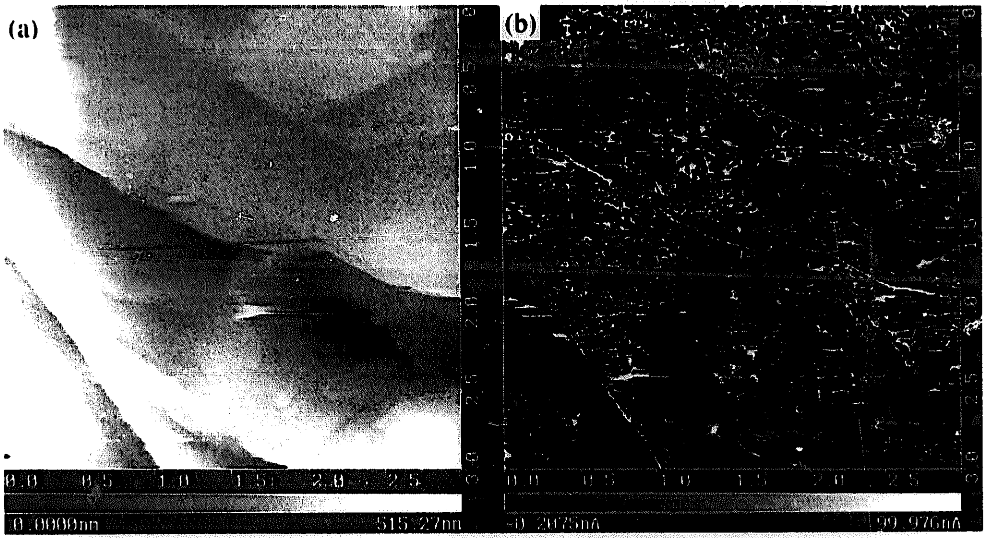

Fig. 7. 3 μm × 3 μm simultaneous (a) contact AFM topography and (b) SCM scans of the KS-44/PVDF (90/10) anode sample. Darker areas in AFM scan correspond to lower areas. Darker areas in SCM scan correspond to low conductivity (PVDF) regions.

that in a larger scan with greater topography changes, the sides of the gold-coated cantilever contacted the sample and, thereby, gave rise to image artifacts.

4. Conclusions

DFM is the optimum SPM mode for topographic imaging of the graphite anode. For large images of over 100 μm, this mode is able to accommodate large changes in the z-height and produces images comparable with those taken by SEM. Using DFM, individual graphite particles and their jagged edges can be effectively imaged with less damage to the sample surface than with the contact AFM.

In the HOPG/PVDF reference sample, every mode used (FFM, LM–FFM, VE–AFM, and SCM) results in images which identified contrasting binder and graphite areas. However, these modes are not equally suited for imaging the practical composite electrode sample. For instance, although SCM is effective for imaging flat surfaces, it cannot be used in large scans which have great changes in topography. Although VE–AFM images of the graphite anode do exhibit image contrast, the boundaries are not as clearly defined as in the other modes and the interpretation of different contrast regions is still debatable. FFM is most effective for determining the location of the few bare graphite areas and the binder-concentrated areas on the graphite anode samples. Since topography changes in the graphite anode do not affect friction images significantly, LM–FFM does not improve the quality of FFM images.

Using the various SPM modes, the structure of the graphite composite anode and the distribution of PVDF binder are both clearly visible. In the graphite/PVDF composite anode, the binder appears to cover in excess of 70% of the graphite surface and is concentrated in numerous islands. These islands are preferentially formed in step structures which are visible on the graphite crystals. Large binder-free exposed graphite areas are visible predominantly on large graphite crystals which contain extremely flat areas. Given this degree of surface coverage, it is indeed surprising that lithium ions are still able to intercalate into the graphite crystals during a charge/discharge cycle.

From this investigation, it is evident that AFM and related techniques are invaluable tools in the observation of actual graphite anode surfaces. This understanding of the various SPM modes for anode topography studies is critical to further topographic investigations of working electrodes.

During the lithium intercalation process, it is well known that a solid electrolyte interface (SEI) forms at the surface of graphite anodes. However, the details and mechanism of this film formation are still not completely understood. Ongoing work will apply the results of this study to in situ electrochemical studies on similar graphite composite anode samples in an attempt to gain a better understanding of this process [10].

References

[1] D. Sarid, *Scanning Force Microscopy*, Oxford University Press, New York, 1991.
[2] E. Gomez, E. Valles, P. Gorostiza, J. Servat and F. Sanz, *J. Electrochem. Soc.*, *142* (1995) 4091–4096.
[3] J. Ruan and B. Bhushan, *J. Tribol.*, *116* (1994) 378.
[4] K. Yamanaka and E. Tomita, *Jpn. J. Appl. Phys.*, *34* (1995) 2879.
[5] R.M. Overney, E. Meyer, J. Frommer and H.-J. Guntherodt, *Langmuir*, *10* (1994) 1281.
[6] M. Inaba, Z. Siroma, Z. Ogumi, T. Abe, Y. Mizutani and M. Asano, *Langmuir*, *12* (1996) 1535.
[7] D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai and H. Yamin, *J. Electrochem. Soc.*, *141* (1994) 603.
[8] G. Binnig, H. Rohrer, C. Gerber and E. Weibel, *Phys. Rev. Lett.*, *49* (1982) 57.
[9] R. Luthi, E. Meyer, L. Howald, H. Haefke, D. Anselmetti, M. Dreier, M. Ruetschi and T. Bonner, *J. Vac. Sci. Technol. B*, *12* (1994) 1673.
[10] K.A. Hirasawa, T. Saro, H. Asahina, S. Yamaguchi and S. Mori, *J. Electrochem. Soc.*, *144* (1997) L81–L84.