Atomic force microscopy on phase-control pulsed force mode in water: Imaging and force analysis on a rhodium-octaethylporphyrin layer on highly oriented pyrolytic graphite

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ABSTRACT

We developed phase-control pulsed force mode (p-PFM) as the operation mode for atomic force microscopy (AFM). The p-PFM allowed us to observe soft or weakly adsorbed materials in a liquid environment using a conventional AFM apparatus, and allowed for force curve mapping (FCM) after offline data processing. We applied the p-PFM to a rhodium-octaethylporphyrin (RhOEP) layer on highly oriented pyrolytic graphite (HOPG), which is applicable to anode catalysts of fuel cells. The RhOEP/HOPG system was stably observed in water by this mode. In the p-PFM image, we found both large and small protrusions, which were not observed in the dynamic force mode, in air. The detailed force analysis suggested that these protrusions are nanobubbles located on the HOPG substrate exposed in holes or pits of the RhOEP layer.

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1. Introduction

Atomic force microscopy (AFM) is an indispensable tool for high-resolution structural or morphological observations of organic molecules and biological materials deposited on well-defined substrates [1–4]. There are various measurement modes in AFM for such systems [5]. In contact mode, a tip is scanned in a transverse direction with constant loading force. Due to the force in the transverse direction, this mode is unsuitable for samples that are easily deformed or weakly adsorbed. These types of samples can be best analyzed in the dynamic force mode (DFM), where a cantilever is oscillated at a frequency close to its resonant frequency and scanned with constant oscillation amplitude. This oscillation avoids drag on the sample in the transverse direction. However, stable observation in liquids is difficult because the viscosity of liquids makes the cantilever oscillations unstable. The sample drag is also avoidable with pulsed force mode (PFM), where a cantilever or a sample is moved up and down with sine waves, and the maximum force during one cycle of the cantilever (or sample) modulation is used as a feedback signal. However, PFM is not suitable to the analysis in liquids because the rapid motion of the cantilever (or sample)

increases the viscosity and prevents the detection of the tip–sample interaction.

In order to attain stable AFM observations of soft or weakly-adsorbed materials in liquids, new measurement modes have been recently developed: Peak Force Tapping (Bruker Corporation) and Jumping Mode + (Nanotec Electronica S.L.) [5,6]. In these modes, the motion of a cantilever is similar to that in PFM, resulting in a continuous series of force–distance curves, and the force at the closest approach position (peak force) is extracted by digital processing. The digital processing enables very small peak forces (typically <100 pN) to be detected under the presence of the viscous force. Therefore, these modes provide stable measurement in liquids, provided the specific AFM apparatuses are available.

In this paper, we examined the application of phase-control pulsed force mode (p-PFM) for soft or weakly-adsorbed materials in liquids without the influence of viscosity. The p-PFM is similar to general PFM except that the phase signal that is measured with a lock-in amplifier is used as a feedback signal. Therefore, the p-PFM can be performed with a conventional AFM apparatus and a lock-in amplifier. We report the result of the p-PFM observations of a Rh-octaethylporphyrin (RhOEP) layer on a highly-oriented pyrolytic graphite (HOPG) in water. Carbon-supported RhOEP is reported to show a high catalytic activity for the electro-oxidation of potential fuels such as CO and borohydride [7,8]. By using the p-PFM, we could eliminate the influence of viscosity and observe
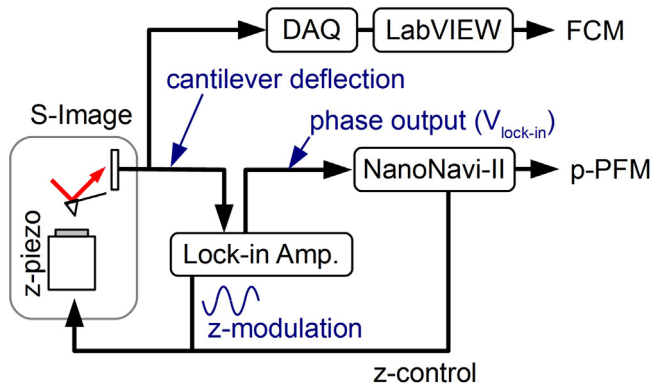
Fig. 1. Schematic of the p-PFM and FCM measurement system.

the RhOEP layer stably in water with a small peak force of several hundred pN. Furthermore, we performed force curve mapping (FCM) on the p-PFM, which revealed the existence of nanobubbles on the RhOEP/HOPG surface [9–11]. The p-PFM, therefore, could be a promising tool for the research and development of environmental and energy devices such as fuel cells, where the understanding of electrode surfaces in liquids is a key issue.

2. Experimental

The AFM apparatus we used is an "S-image" with a "NanoNavi-II" controller (Hitachi High-Tech Science Corporation). For the phase measurement in the p-PFM, a lock-in amplifier "LI5640" (NF Corporation) was used. Data acquisition for FCM was performed with a data acquisition interface (DAQ) "USB-6216-BNC" (National Instruments Corporation). The acquired data were treated with the original software developed by LabVIEW (National Instruments Corporation). The obtained images were processed with the programs of GWIDDION and WSxM [12].

We performed three AFM modes, the DFM, SIS-AFM, and p-PFM. The DFM and SIS-AFM modes were provided by the NanoNavi-II controller, and the SIS-AFM mode was developed by Hitachi High-tech Science [13]. This mode is based on contact mode, and a tip approaches the sample only while acquiring data and is retracted while moving to the next sampling point, thus preventing sample drag. The p-PFM mode was developed in our laboratory and was performed by the following procedure. The sample z-position was modulated by a sine wave with an amplitude of 100–200 nm_{p-p} and a frequency of 0.5–1 kHz. The cantilever deflection signal was put into the dual-phase lock-in amplifier, and subsequently the phase output signal of the lock-in amplifier ($V_{lock-in}$) obtained with a time constant of 0.3–1 ms was inputted into the controller as a feedback signal (Fig. 1).

The FCM measurement was performed on the p-PFM. The force signal, simultaneously obtained with a p-PFM image, was acquired by a computer through the DAQ and the tip–sample interaction was extracted by offline processing from the force signal using our original software. The FCM data were then obtained as a dataset of force curves (force–displacement curves) at each pixel of the p-PFM image. Generally, FCM based on the contact mode is very slow because the force curve measurement at each image pixel typically takes more than 100 ms, requiring more than 1.5 h for an image with 256 × 256 pixels. Conversely, a force curve in the FCM on the p-PFM was obtained during one cycle of the sample modulation (typically 1 kHz), and was therefore much faster than the general FCM. The acquisition time is dependent on the sampling speed of the DAQ used. The sampling speed of our DAQ was 100 kS/s. To obtain 100 samples at each pixel point, the modulation frequency was set to 1 kHz. Therefore, the scanning

rate was limited to approximately 2 ms/pixel, which corresponded to an acquisition time of approximately 5 min.

The cantilevers used were SI-DF3 (spring constant $k = 1.6$ N/m, resonant frequency $\omega_0 = 23$–31 kHz, material: Si) and SN-AF01-S-NT ($k = 0.1$ N/m, $\omega_0 = 34$ kHz, Si_3N_4) purchased from Hitachi High-Tech Science. The RhOEP layer was formed on the HOPG substrates The RhOEP molecules were dissolved in CH_2Cl_2 at a concentration of 0.7 mM. A cleaved HOPG substrate was immersed in the solution for 1 min, and rinsed with pure CH_2Cl_2. The AFM observations were performed in air or water. The water used was distilled water without any further treatment such as gas saturation or degassing.

3. Results and discussion

3.1. Analytical consideration of p-PFM

We analytically considered the phase difference $\Delta\varphi$ between the viscous force and the tip–sample interaction. First, we considered the motion of a cantilever in a liquid without any tip–sample interaction. When the cantilever beam end is moved up and down with an amplitude A and a frequency ω at some height u_0, the motion of the cantilever can be described as a function of the tip–sample distance z and the cantilever deflection a:

$$m\frac{d^2z}{dt^2} + \gamma\frac{dz}{dt} + ka = 0 \tag{1}$$

$$z = u_0 + A\cos\omega t + a \tag{2}$$

where m is the effective mass of the cantilever, γ is the coefficient of viscosity, and k is the cantilever spring constant (Supplementary material, Fig. S1). From Eqs. (1) and (2), the motion of the cantilever deflection can be obtained as

$$a = \frac{A\omega\sqrt{c^2 + \omega^2}}{\sqrt{(\omega_0^2 - \omega^2)^2 + c^2\omega^2}}\cos(\omega t - \alpha - \beta)$$

$$\tan\alpha = \frac{c}{\omega}$$

$$\tan\beta = \frac{c\omega}{\omega_0^2 - \omega^2}$$

where $c = \gamma/m$, and $\omega_0^2 = k/m$. Setting $Q = \omega_0/c$, $\tan\beta$ can be expressed as

$$\tan\beta = \left(\frac{1}{Q}\frac{\omega}{\omega_0}\right) / \left(1 - \left(\frac{\omega}{\omega_0}\right)^2\right).$$

By substituting typical values of a cantilever resonant frequency, a sample modulation frequency, and a previously reported Q-factor in water ($\omega_0 = 30$ kHz, $\omega = 1$ kHz, $Q = 1$), β was calculated to be 0.033 (1.9°), indicating that we can consider $\beta \approx 0$ in the p-PFM. The phase of the viscous force was then obtained as $\alpha = \tan^{-1}(c/\omega)$. Next, we considered the repulsive tip–sample interaction. If the sample is hard enough, the motion of the cantilever deflection may be given as

$$a = A\cos(\omega t - \pi).$$

Finally the phase difference $\Delta\varphi$ was obtained as

$$\Delta\varphi = \pi - \tan^{-1}\frac{c}{\omega}. \tag{3}$$

In the experiment, we modulated the sample instead of the cantilever, and the cantilever deflection was caused by the oscillation of water induced by the sample modulation. In spite of such difference, Eq. (3) reproduced the experimental results well as described