Application of dynamic impedance spectroscopy to atomic force microscopy

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Abstract
Atomic force microscopy (AFM) is a universal imaging technique, while impedance spectroscopy is a fundamental method of determining the electrical properties of materials. It is useful to combine those techniques to obtain the spatial distribution of an impedance vector. This paper proposes a new combining approach utilizing multifrequency scanning and simultaneous AFM scanning of an investigated surface.

Keywords: atomic force microscopy, dynamic electrochemical impedance spectroscopy, non-stationarity

1. Introduction
Since its development [1], atomic force microscopy (AFM) has found application in many scientific fields such as life sciences [2–5], materials engineering [6–10] and physics [11]. On the other hand, impedance spectroscopy is one of most important techniques for determining the electrical properties of materials [12–18]. Important scientific possibilities offered by the above-mentioned techniques prompted worldwide effort to combine them. Fundamental research in this field was documented by Kalinin et al [19–21] and O’Hayre et al [22, 23]. Two distinct techniques were proposed, namely, impedance imaging and spectroscopy. In the former, a single frequency is applied and, during the AFM scanning of the surface, the distribution of impedances for a given frequency is obtained. In the latter, the impedance in the assumed frequency range is obtained. For this purpose, the frequency obtained by the frequency method must be applied, which necessitates the use of sequential AFM for stationary tip localization.

This paper proposes a combination of those techniques, i.e. performing AFM scan with simultaneous acquisition of multifrequency impedance spectra. In order to implement this scheme, the following modification is suggested. Instead of using single-frequency voltage, a package of superimposed sinusoids of selected frequencies, amplitudes and phases is applied. Assuming the linearity of the investigated system, the current response should be a linear combination of particular frequency responses.

The impedance of the studied surface can change during the scan altering the spectral structure of the recorded current response and thus the impedance. This limits application of Fourier analysis to obtain impedance spectra [24]. We believe the joint time-frequency methods of signal analysis should be applied in order to properly correlate impedance characteristic with the properties of the investigated surface.

2. Theoretical assumptions
Figure 1 presents the scheme of impedance measurements. The AFM tip is moving with a linear speed \( V \). The vicinity of every scanning point is perturbed during a given time by a potential signal introduced between the tip and the sample by means of a waveform generator and a potentiostat. The frequency generator provides an alternating voltage signal of assumed spectral composition. The frequency analyzer is responsible for the synchronous acquisition of perturbation and response signals and their processing to obtain the impedance. The suggested modification to the classical technique in this article involves the application of a
The moving analysis window \( h(\tau) \), whose values are equal to zero beyond a given time interval (window length). The actual position of the window in the time domain is represented by the term \( h(\tau - t) \). For each displacement of the window \( h(t) \), a portion of the signal with a length \( h(t) \) is Fourier transformed thus yielding a function \( G(f, t) \), which depends on frequency and time.

Applying STFT to recorded voltage perturbation and current response yields two transforms \( U(f, t) \) and \( I(f, t) \), respectively, which determine the time-dependent impedance:

\[
Z(f, t) = \frac{U(f, t)}{I(f, t)}. \tag{4}
\]

Provided that AFM scanning is performed at a defined rate, with a synchronous acquisition of current and potential, the impedance signal \( Z(f, t) \) can be easily correlated with the movement of the tip across the studied surface.

3. Experimental details

We used Nanoscope V AFM (Digital Instruments) coupled to an impedance measurement system and Veeco anisotropic DDES-P-10 probes. The probe parameters are: tip height 10–15 μm, front angle 25°, side angle 22.5°, nominal tip radius 35 nm, contact layer –100 nm of doped diamond (further information available on the manufacturer’s web pages). The impedance measurement system consists of a KGLstat 4.1 potentiostat working in a two-electrode configuration, providing flat power characteristic without significant phase distortions for frequencies up to 50 kHz. The structure of the sinusoidal package is provided in table 1. The package was optimized to obtain a minimal value of the maximal instantaneous value (decreased from 92.57 mV without phase optimization to 66.80 mV). The sampling rate of the current and potential signals was 125 kHz. The alternating potential perturbation is the sum of 20 sine waves of optimized frequencies and amplitudes (table 1) generated using a DXI 6120 measurement board (National Instruments). The frequencies, phase shifts and amplitudes are listed in table 1. The perturbation was applied between the scanning tip and a sample gold base, and the current response along with the perturbation signal was recorded. The measurement procedure was controlled using LabVIEW software. The analyzed sample was a quartz plate with a deposited gold film in the form of a 5 mm-diameter circle. The gold base was partially covered with a Prussian Blue layer [33] by chronovoltamperometry (\( \frac{dE}{dt} = 5 \text{ mV s}^{-1} \)) performed in a 0.75 mM FeCl₃/0.75 mM K₃[Fe(CN)₆] solution in 0.5 M KNO₃ in the potential range –0.2 to 0.35 V. The solution was prepared using p.f.a.-grade reagents and deionized water.

4. Results and discussion

Figure 3 shows an image of the gold substrate with electrolytically deposited zeolitic structures of Prussian Blue. The sample was scanned at a rate of 1 Hz with an atomic
force microscope coupled to a system for dynamic impedance measurement. AFM and impedance scans were performed in two separate systems correlated by the clock signal issued by AFM after each line. The current and potential signals can be simultaneously acquired at a rate specific for a DAQ card (up to 700 kHz in the case of DXI 6120); however, the scanning capability of AFM is not related to the DAQ sample rate.

A horizontal line in figure 3 marks an area selected for processing the perturbation and response signals. The rectangular analysis window in the STFT procedure had a size of 1250 × 1250 points. The time-frequency distribution of the obtained impedance results is closely related to the window size. For a given sampling frequency \( f_s \), frequency resolution is defined as \( \Delta f = f_s / N \), where \( N \) is total number of points. Large window usually results in small dispersion of the frequency band corresponding to the sinusoidal (periodic) components and poor resolution of the pulses. Besides, the signal is spread over larger number of points that decreases its intensity. Small window improves resolution in the time domain, but the spatial sampling deteriorates. Thus there is a compromise between the spatial resolution of impedance data (time-domain impulses reflect abrupt changes in the recorded current waveform, generated by changes of electrical properties of surface) and the frequency resolution of each impedance spectrum.

A series of impedance spectra with a spatial resolution of 586 nm were obtained (figure 4). The impedance spectra were calculated for each of the two pixels of a scanned image obtained at a resolution of 256 points per line. The image

Table 1. Parameters of perturbation package used in the dynamic impedance measurement.

| Frequency (Hz) | Phase (deg) | Amplitude (V) |
|---------------|-------------|---------------|
| 700           | 198.58      | 0.01          |
| 1100          | 352.048     | 0.01          |
| 1700          | 76.5354     | 0.0099        |
| 2300          | 52.5972     | 0.0098        |
| 2900          | 199.428     | 0.0098        |
| 3700          | 175.779     | 0.0097        |
| 4100          | 171.638     | 0.0096        |
| 4700          | 263.644     | 0.0095        |
| 5300          | 167.228     | 0.0095        |
| 5900          | 133.26      | 0.0094        |
| 6700          | 232.899     | 0.0093        |
| 7900          | 28.6269     | 0.0092        |
| 9700          | 195.414     | 0.009         |
| 12700         | 55.263      | 0.0086        |
| 15100         | 300.441     | 0.0084        |
| 19100         | 293.217     | 0.0079        |
| 23300         | 227.749     | 0.0074        |
| 29300         | 141.513     | 0.0068        |
| 35900         | 195.815     | 0.006         |
| 44900         | 35.301      | 0.005         |
sampling was 1 Hz, while single impedance spectrum was recorded within 0.01 s. These parameters were sufficiently fast for local stationarity.

An abrupt change in the obtained impedance spectra is observed. For the scan range corresponding to the gold layer (0–33.4 µm), the impedance exhibits purely resistive character, while the Prussian Blue layer shows capacitive character with capacitance and resistance connected in series. The surface topography was correlated with the parameters of fitted impedance equivalent circuit using ZSimpWin software. Figures 5(a) and (b) show changes in the mentioned parameters and the corresponding profile heights along the studied cross section.

The detected changes in electrical parameters are well correlated with the changes in the surface profile. Unfortunately, the measurements in the contact mode significantly decrease the lifetime of conductive tips. This problem substantially limits the number of acquired data and should be solved to provide a wider application of the presented scanning technique.

The last important issue is the suitability of dynamic impedance spectroscopy for investigating nonstationary electrochemical systems. If the properties of a given object change in time then the measurement period should be shortened to ensure pseudostationary conditions. In the presented case, impedance characteristics were obtained using the perturbation package of the frequency composition presented in table 1. Assuming seven repetitions of the fundamental period (determined by the length of the analysis window), the time required to collect a single spectrum is $7/f_0 = 0.01$ s. The remaining components, whose frequencies are multiples of the fundamental frequency $f_0$, are acquired simultaneously with the slowest one; thus, the total time is unchanged. Meanwhile, acquisition of the same spectrum using traditional frequency by frequency method requires a time equal to the sum of 20 intervals of $7/f_i (i = 0, \ldots, 19)$ that gives 0.038 s for a single measurement. A four-fold decrease in measurement time using our technique is significant.

5. Conclusions

This paper suggests a novel approach to the coupling of dynamic impedance measurement with atomic force microscopy. A system is proposed allowing multifrequency impedance measurement during simultaneous surface scanning. The authors present methodology for obtaining time-dependent and spatially resolved impedance spectra using short-time Fourier transformation.
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