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Acoustic sensors for the control of liquid–solid interface evolution and chemical reactivity

J.Y. Ferrandis [a], S. Tingry [b], J. Attal [a], P. Seta [b,*]

[a] LAIN, UMR CNRS 5011, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex, France
[b] IEM, UMR CNRS 563, 1919 Route de Mende, 34293 Montpellier Cedex 5, France

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Abstract

Less classical than far-field acoustic investigations of solid materials and/or solid–liquid interfaces, near-field acoustic properties of an acoustic solid wave guide (tip), thin enough at its termination to present an external diameter smaller than the excitation acoustic wave wavelength, is shown to be able to probe interface properties. As a result of that, these near-field acoustic probes can play the role of chemical sensors, if chemical modifications or chemical reactions are concerned at their surface. In that context, a chemical sensor was realized by electrochemical deposition of an electron-conducting polymer (polypyrrole–biotin) on a metal tip, followed by enzyme attachment by molecular recognition process involving the biotin–avidin-specific interaction. Results from near-field acoustic showed that the enzyme modification of the polymer layer can be detected by this new acoustic sensor.

Keywords: Acoustic near field; Interfacial phenomena; Chemical sensor; Enzymes recognition

1. Introduction

Far-field acoustic echography is frequently used to make images of the surface of materials and to probe their inner phase properties, as this method is non-invasive and allows in situ investigations on non-optically transparent systems. Since a few years in parallel to this classical technique, a new acoustic means of probing liquid media more or less viscous media called near-field acoustic (NFA) technique has been developed [1]. The acoustic beam issued from the source is confined in a cylindric acoustic wave guide presenting a termination (tip), thinned enough, so its end diameter is far smaller compared to the wavelength of the guided acoustic wave (Fig. 1). In the latter case, the probed area is localized and the spatial resolution of the probing system is of the order of magnitude of the size of the tip. This technique of acoustic resonance is directly inspired of AFM and STM techniques which combine concepts of spatial resolution associated to the size of the tip.

The NFA sensor is an oscillating system that uses the alterations of the resonance state of an acoustic horn as a function of the evolution of the mechanical properties of the medium in which the terminal part, the tip, is immersed (see Experimental). The elastic wave is transmitted to the horn by a piezoelectric transducer fed with a low-frequency sinusoidal electrical signal (around 50 kHz). Because the tip is much smaller than the wavelength, the sensor operates in near-field conditions. This resonating system is very sensitive to the medium in contact with the probe. For the horn, the external medium constitutes a mechanical load that modifies its resonance state, so the acoustic signal is altered by the interaction between the probe and the medium. This involves a variation in the electrical signal at the transducer. In return, the study of the electrical resonance state provides information on the medium in which the probe is immersed.

The alteration of the interface (for instance, the dynamics of organization, or because of a reactivity leading to a new chemical state of the interface) modifies the impedance of the resonating system. Then it appears to be possible to follow this interface by measuring the impedance of the sensor.

Hence, it is possible to follow interfacial properties of a system that are modified with time, either because of a change of the material itself (for instance, the dynamics of organization) or because of a reactivity leading to a new chemical state of the interface. This type of probe becomes an indicator by the acoustic 'signature' of the change in the chemical parameters of its surface and/or of its volume due to the involved

* Corresponding author. Tel.: +33 4 67613389; fax: +33 4 67042820.
E-mail address: pseta@iemm.univ-mntp2.fr (P. Seta).

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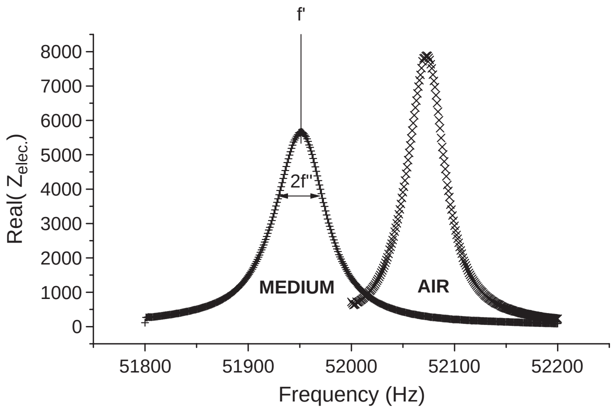

Fig. 1. Determination of the two parameters measured by applying a frequency ramp to piezoelectric element: the frequency shift of the resonance f' and the half width of the resonance f''.

phenomenon, leading us to propose the name of "chemical acoustic sensor" to such device. This behavior opens a wide field of applications of the latter device as sensor of chemical processes like recognition phenomena.

The general trend of the presented work will be to show that it is feasible to detect, using this near-acoustic field approach, the alteration of the resonance curve due to the alteration of the mass of the tip by surface chemical reaction.

In order to evidence this concept, we applied the NFA technique to the probing of the immobilization of enzymes into a membrane layer-type material elaborated as surface coverage of the tip. The enzymes have been incorporated into the surface tip layer by the well-known molecular recognition process that involves the association (formation of a molecular complex) between biotin and avidin. This complex is thermodynamically very stable as the association constant of the process is $K_m = 10^{15}$ M^{-1} [2].

2. Experimental

2.1. Chemicals

Avidin (chromatographically purified), biotin-labeled glucose oxidase (B-GOD) (E.C. 1.1.3.4.) from *Aspergillus niger* (108 U mg^{-1}) were purchased from Sigma.

The buffer was prepared from potassium monobasic and dibasic phosphate salts (pH = 7) from Aldrich. All the aqueous solutions were prepared using 18 MΩ cm MilliQ water (Millipore). Pyrrole monomer and acetonitrile were purchased from Aldrich, $NaClO_4$ from Merck. The pyrrole–biotin monomer was a generous gift from S. Cosnier at LEOPR (Joseph Fourier University, Grenoble, France), whose synthesis was described elsewhere [3].

2.2. Apparatus

2.2.1. NFA sensor

The scheme of the NFA system is shown in Fig. 2.

The tip A made of stainless steel is a rod of 1 mm in diameter and a few centimeters in length. The resistor (1 MΩ) allows the

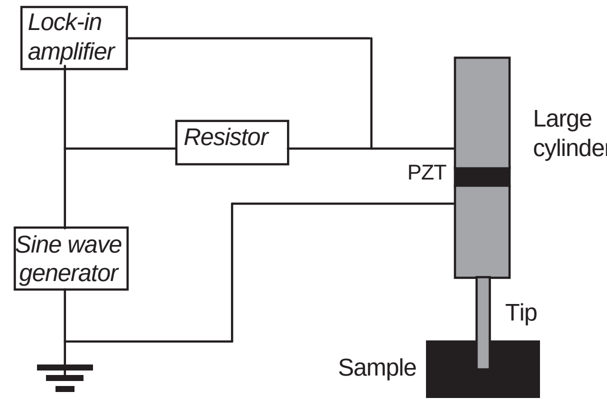

Fig. 2. Sensor geometry and electric circuit.

lock-in amplifier to measure the electrical impedance of the piezoelectric transducer (PZT). A frequency scan gives the real part of the electric impedance Z_{elec} vs. frequency. The parameters measured are: f' (frequency in the analysed medium) and f'' (half width of the resonance peak) (Fig. 1).

The mechanical impedance of the immersed part of the tip A is then calculated:

$$Z_{mech} = \frac{\text{Strain in the section of the tip A at the surface of the sample}}{\text{Velocity of deformation in this section}}.$$

This impedance (a complex number) describes precisely the interaction between the medium and the sensor. The imaginary part of the impedance is related to the standing waves in the medium, and the real part to the energy dissipated in the medium. The external part of the sensor is a resonant system by itself, whose frequency is determined by its size and by the above impedance Z_{mech}. By means of a simple 1D scheme (all the waves can be considered in one dimension) [4] (Fig. 1), the electric impedance Z_{elec} across the piezoelectric element can be deduced at each frequency f.

2.3. Electrochemistry

Electrochemical experiments were carried out in a classical three electrodes cell using a home-made counter-electrode in

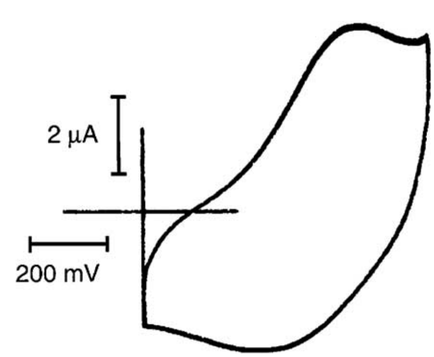

Fig. 3. Cyclic voltammetry of the polypyrrole–biotin film deposited on a stainless steel tip in water 0.1 M $NaClO_4$ as electrolyte, 50 mV/s, vs. $Ag/AgNO_3$ electrode.