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Combination of nanogravimetry and visible spectroscopy: A tool for the better understanding of electrochemical processes

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ABSTRACT

A new, software controlled electrochemical measuring system for the simultaneous measurements of surface mass changes and optical absorbance spectra has been developed. A usual EQCN apparatus with transparent ITO covered quartz crystal working electrode was built in a three-electrode cell made of polyvinylidene fluoride. A detailed description of both the apparatus and the software are given in the paper. The system was tested by the deposition and electrochemical transformation of polyaniline films. A new insight into the properties of the system is given by introducing the molar absorptivity based on simultaneous mass an absorption measurements.

1. Introduction

Electroanalytical chemistry has seen tremendous developments in the last decades. Especially the combinations of electrochemical and non-electrochemical methods (e.g., radioactive labeling, optical spectroscopy, paramagnetic resonance spectroscopy, mass spectrometry, scanning probe and electron microscopy, analysis methods based on synchrotron radiation) lead to more precise quantitative and qualitative evaluation of electrode processes [1–3].

Due to its capability of detecting surface mass changes up to a sensitivity of a few ng/cm^2 simultaneously with potential or current variations, e.g., during a cyclic voltammetric experiment, the electrochemical quartz crystal nanobalance (EQCN) became a widely used *in situ* technique. By using an EQCN, extremely useful quantitative information about electrode processes such as adsorption, deposition and dissolution, ion and solvent exchange between the surface film and the solution can be obtained. Based on the mass change and the charge mechanistic conclusions can be drawn. However, by using EQCN only the total mass change can be measured even in the case of ideal behavior, i.e., when other effects, e.g., stress, viscoelasticity do not influence the measured frequency changes. Therefore, one can draw reliable conclusion concerning the mechanism, if the nature of the intermediates and products of the electrochemical reactions will be determined by an independent technique. If the formed products or intermediates are colored species, ultraviolet–visible (UV-VIS) spectroelectrochemistry, i.e., the combination of any electrochemical technique with UV-VIS spectroscopy is a plausible choice. The coupling of the EQCN technique with spectroscopic UV-VIS measurements certainly helps to solve this problem. In many studies both nanogravimetric and spectroscopic techniques combined with electrochemistry have been used, however, in separate experiments. This approach is not always satisfactory since even at the same potential value or potential cycling conditions the state of the surface film may not be the same. In order to combine the mentioned techniques, we constructed a software controlled electrochemical measuring system. In the present paper we introduce our newly developed hyphenated measurement system and demonstrate its usability.

There have been attempts previously to combine EQCN with UV-VIS spectroscopy. First, a light beam either reflected [4,5] or at grazing incidence [6] was used. Shimazu et al. [7] disseminated their research in the form of a preliminary note, there is a lack of drawings of the experimental setup and they did not make use of the corresponding frequency and absorbance data, but treated them separately. Xie et al. [8] used a gold-covered quartz crystal in such a way that only the front surface was covered with gold to diminish the absorbance, and it formed also a part of the wall of the cell. The other side of the crystal was in contact with an electrolyte and a platinum wire immersed in this solution connected the quartz crystal to the oscillation circuit. Kim et al. [9] used an *in situ* approach to simultaneously detect mass change and absorption spectra of a polypyrrole thin film. They used two ITO crystals in their double channel spectrophotometer: one as a reference probe, and the other as a working electrode. EQCN has been

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combined with other spectroscopic methods, like ellipsometry [10] or FTIR [11,12] as well.

Polyaniline, a thoroughly studied conducting polymer [13,14] with well-known EQCN [15] and UV-VIS spectroscopic [16–18] characteristics was deposited on our ITO–EQCN electrode in order to demonstrate the unique features of our new measuring system. Polyaniline has (i) a pronounced color transition accompanying its oxidation and reduction reactions; (ii) the mass changes during the deposition of the polymer are easily detectable; and (iii) the ingress and egress of charge compensating ions may also cause a significant mass change.

The method presented herein makes the simultaneous acquisition of electrochemical, nanogravimetric and vis spectroscopic data possible. The so-obtained independent parameters help to elucidate the behavior of various electrochemical systems and to characterize them in a more detailed way. The ease of use of the method compared to the wealth of complementary information it gives, is promising for widespread applications not only in the field of conducting polymers, but also in any other electrochemical experiments where colored (or light emitting) species appear.

This paper discusses the development phases of the hardware and software parts of the system and demonstrates its capabilities for studying electropolymerization reactions. Based on the corresponding adsorption and frequency changes yielded by the measured multidimensional dataset, the analysis of a special extinction coefficient (molar absorptivity) is presented together with a promising application.

2. Experimental

Analytical grade H_2SO_4 (Merck) was used as received. Aniline (Merck) was freshly vacuum distilled from Zn powder before use. The electropolymerization was executed by potential cycling using a solution containing 0.01 mol dm^{-3} aniline and 0.1 mol dm^{-3} H_2SO_4. This solution is colorless when freshly prepared. Doubly distilled water was used throughout the experiments.

5 MHz AT-cut crystals of one inch diameter coated with indium tin oxide (ITO) served as working electrode (Microvacuum Ltd., Budapest, Hungary). The electrochemically and the piezoelectrically active areas were equal to 1.37 cm^2 and 0.4 cm^2, respectively. The electrochemical and spectroscopic properties of the electrodes were examined and the results together with the electrode geometry can be seen in Fig. 1.

A three-electrode cell with a platinum wire as counter electrode and a sodium chloride saturated calomel electrode as the reference electrode was used. The details of instrumentation are described in Section 3.2.

3. Results and discussion

3.1. Theoretical considerations about EQCN and UV-VIS spectroscopy

EQCN is a piezoelectric device comprising an appropriately cut quartz crystal covered both sides with thin conducting layers [19]. It is commonly used as a mass sensor based on the assumption that a linear relationship exists between the Δf change in the resonance frequency of the crystal and the mass change per unit area (Δm) occurring at its surface [20]:

$$\Delta f = -C_f \cdot \Delta m, \qquad (1)$$

where C_f is the integral sensitivity of the crystal. In case of many electrochemical systems, however, Eq. (1) does not provide a good approximation of the real mass changes of the surface. In such cases the use of other models or complementary information accessible is required for data interpretation.

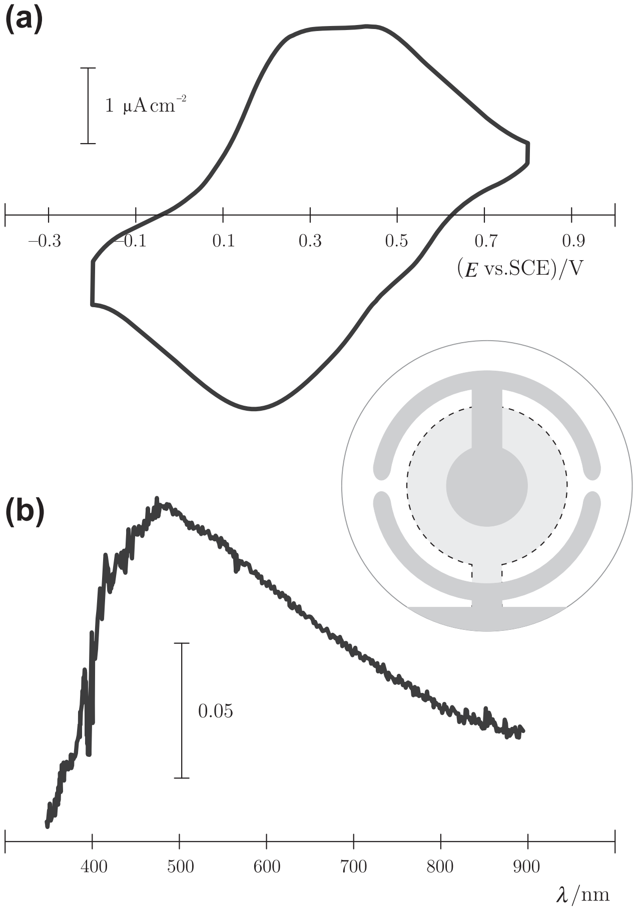

Fig. 1. Cyclic voltammogram and absorbance spectrum characteristic to bare ITO–EQCN electrodes. Scan rate: 10 mV/s, electrolyte: 0.1 mol dm^{-3} H_2SO_4. The drawing shows the geometry of the crystal and the deposited ITO.

Vis spectroscopy uses the visible range of the electromagnetic radiation to obtain qualitative, structural and quantitative information about the absorbing species. This method may be applied to investigate both the liquid and solid phases of the electrode. With conventional transmission experiments using optically transparent electrodes, the reactant dissolved in the liquid phase should not adsorb light in the wavelength window of the deposited product. However, if EQCN data are measured simultaneously with the UV-VIS spectra, it becomes possible to distinguish between species absorbing in the solution and at the electrode surface.

To relate the absorption of light to the concentration of species, usually the expression known as Beer–Lambert law is used. It states, that the absorbance (A) is a linear function of the concentration (or number density) of absorbers (c) and the distance (i.e., the thickness of the absorptive layer) the light travels through (ℓ). In mathematical form:

$$A = \varepsilon \cdot c \cdot \ell, \qquad (2)$$

where ε is the molar absorptivity (extinction coefficient) of the absorber.

To relate the independently measured absorbance (intensity) and frequency, data let us consider the following principles. The quartz crystal nanobalance in its original, non-electrochemical form was used to measure layer thickness of different metals deposited from gas phase. Sauerbrey constructed Eq. (1) in relation to that use [20]. According to (1), the layer thickness (i.e., the deposited surface mass, assuming homogeneous density and