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A new method for characterizing the growth and properties of polyaniline and poly(aniline-co-*o*-aminophenol) films with the combination of EQCM and in situ FTIR spectroelectrochemisty

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Abstract

A new method of in situ piezoelectric Fourier transform infrared (FTIR) spectroelectrochemisty, i.e., the combination of in situ FTIR and electrochemical quartz crystal microbalance (EQCM), was developed to study the electropolymerization of aniline and aniline-co-*o*-aminophenol, to investigate the properties of the polymers in 0.2 M $HClO_4$. The piezoelectric electrochemical studies showed that the copolymerization process was changed in the presence of *o*-aminophenol and the copolymer exhibited different electrochemical behaviors from polyaniline and poly-*o*-aminophenol. The effects of the molar ratio of *o*-aminophenol on the copolymerization speed and the scan rate or pH values on the electroactivity of the copolymer were also investigated. The results suggested that the copolymer formed in the case of $F = 0.1$ had good stability and electroactivity than polyaniline at different pH values. The results obtained by the way of in situ piezoelectric FTIR spectroelectrochemisty indicated that the copolymerization process and the properties of the copolymer were different from that of polyaniline. The polymerization mechanisms and the structure of the two polymers were also different from each other. The copolymer formed through head-to-tail coupling of the two monomers via ─NH─ groups was a new polymer rather than a mixture of polyaniline and poly-*o*-aminophenol.

Keywords: In situ piezoelectric FTIR spectroelectrochemisty; EQCM; Copolymerization; Aniline; *o*-Aminophenol

1. Introduction

Polyaniline has been widely studied [1–4] due to its high conductivity, excellent electrochromic property, good redox reversibility and stability in aqueous solutions. However, its practical applications are limited at certain degree for its intractable nature, e.g., its insolubility in some solvent and low conductivity in solution of pH > 4. A lot of work has been conducted to solve these problems by the polymerization of aniline derivatives with sulphuric acid group [5–7], alkyl group [8,9] or carboxyl group [10,11] substitutions. But such substituted polyaniline films generally have lower conductivity than the original polyaniline films. In order to obtain polymers with higher conductivity and better solubility, copolymerization methods of aniline with its derivatives were developed [12–16]. Electrochemical copolymerization of aniline with *o*- or *m*-toluidine was conducted by Wei et al. [17], and the results showed that the conductivity of the copolymer could be controlled in a broad range. Poly(aniline-co-*m*-aminobenzenesulphonic acid) has been successfully used for fabricating the secondary Zn-copolymer battery [18]. Copolymerization of aniline with diphenylamine [19] and dithiodianiline were also studied [20]. These successful work mentioned above indicated that the properties of the copolymer possessing polyaniline-like structure are similar to the parent polyaniline, and could be strongly affected by the sort of the monomers and their molar ratios.

On the other hand, the oxidation of *o*-aminophenol on different electrode materials (platinum, gold, carbon, etc.) in aqueous acid media was studied and shown to form an electroactive polymer [21–23]. The electrochemical and electrochromic properties of the polymer have been studied [22–24] and the polymer was applied to fabricate sensors [25,26] and to deposit metals [27].

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Owing to the good properties of polyaniline and poly-*o*-aminophenol, the copolymerization of these two monomers may produce excellent new materials. And recently, Mu reported that poly(aniline-co-*o*-aminophenol) exhibited good electrochemical activity, excellent stability and high reversibility in pH 5.0 [28]. Due to these properties, the copolymer was used as sensor for detecting catechol [29] and uricase [30]. However, all of these papers were failed to study the formation mechanism of the copolymer, which is surely an important aspect for understanding the properties of the copolymer.

By using electrochemical method, only electrical parameters were obtained. These parameters, such as potential, current, impedance, electric charge and so on are to be used for elucidating the electrochemical reaction mechanism or quantitative analysis. But these parameters are not enough if we try to thoroughly clarify the mechanism of an electrochemical process and the electrochemical properties of a material. Fortunately, the information from quartz crystal microbalance (QCM) and simultaneous spectral measurements can provide more complete and real-time information, thus leading to less ambiguity in description of a practical electrochemical process.

Electrochemical quartz crystal microbalance (EQCM), a powerful tool to monitor the mass change on the electrode, has been used to study the deposition of polymer [31] and metal [32]. The Sauerbrey equation that describes a frequency–mass relationship for load or removal of a rigid and thin film [33] is given as follows:

$$\Delta f_0 = -2 f_{0\mathrm{g}}^2 \frac{\Delta m}{A\sqrt{\rho_\mathrm{q}\mu_\mathrm{q}}} = -2.264 \times 10^{-6} f_{0\mathrm{g}}^2 \frac{\Delta m}{A} \qquad (1)$$

where Δf_0 and $f_{0\mathrm{g}}$ are the frequency shift and the fundamental frequency of the quartz crystal in Hz, respectively, Δm the mass loaded on the electrode in grams, A the geometric area of the electrode in cm^2, ρ_q the density of quartz (2.65 g/cm^3) and μ_q is the shear modulus of quartz (2.947×10^{10} dyn/m^2). For the crystal used in this work ($f_0 = 9$ MHz), a frequency change of ±1 Hz corresponds to a mass change of ±5.5 ng/cm^2 (minus/plus means increase/decrease, respectively). Identification of species related to the electrochemical reaction should be performed by using some spectroscopic measurements. Up to now, the combination of EQCM with spectroscopic measurements has been greatly developed by several research groups, such as EQCM combination with in situ UV–vis [34], fiber-optic reflectance [35] or ellipsometry [36]. Compared with the wide utilizations of the combining technique of EQCM with these spectrum technique, only one paper by Shimazu et al. [37] has been found so far to report the powerful approach of simultaneous EQCM in combination with in situ FTIR technique, In the paper, Shimazu reported that they carried out simultaneous detection of structural change and mass transport accompanying the redox of ferrocenylundecanethiol mono layer with the FTIR reflection absorption spectroscopy/electrochemical quartz crystal microbalance combined system. However, due to the limitation of their experimental approach, Shimazu only recorded the resonance frequency with a frequency oscillator and obtained no other piezoelectric parameters about the film. In addition, they did not monitor the in situ synthesizing process of the film as well. Furthermore, the quartz crystals used for the EQCM studies were not polished and thus the simultaneous spectroelectrochemical measurement in the mirror reflectance mode at a raw piezoelectric quartz crystal (PQC) electrode may suffer from low optical sensitivity, since the reflectance beams may be scattered and many of them could hardly be collected into the optical detector.

In this paper, attentions were paid to the combination of EQCM with Fourier transform infrared reflection absorption spectroscopy (FTIR-RAS), since FTIR-RAS can provide information regarding both the orientation of chemical functional group and mode of bonding of the absorbent on electrode surfaces [38]. Such information as well as mass transport is important for understanding the electrochemical processes on modified electrode [39]. The combination of piezoelectric quartz crystal impedance with in situ FTIR spectroelectrochemisty, i.e., in situ piezoelectric FTIR spectroelectrochemisty is further developed and used to study the polymerization of aniline and aniline-co-*o*-aminophenol and to investigate the properties of the polymers.

2. Experimental

2.1. Apparatus and chemicals

The experimental device is illustrated schematically in Fig. 1A. Electrochemical experiments were performed with a CHI660 A electrochemical workstation (CH Instruments Co., USA) controlled by CHI660A software. A research quartz crystal microbalance (RQCM, Maxtek Inc., USA) controlled by Maxtek RQCM software. The RQCM is able to record the resonant frequency (f_0) and the motional resistance (R_1) of the crystal

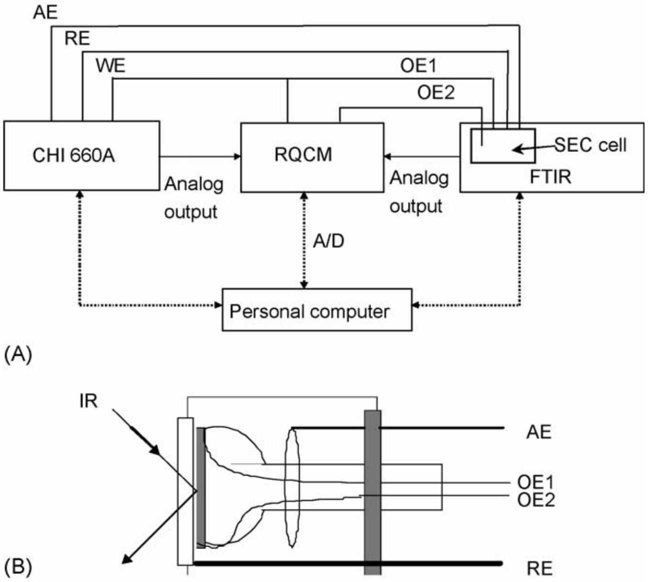

Fig. 1. (A) The EQCM-FTIR setup and (B) its spectroelectrochemistry cell. WE, the work electrode; RE, Ag/AgCl reference electrode; AE, auxiliary electrode; OE1, oscillation electrode 1 (Au, in air); OE2, work electrode 2 (Au, contacting solution).