

Scientific paper

Impedance Scanning QCM Studies of Aniline Electropolymerization in Aqueous Phosphoric Acid Solutions to Determine the Most Effective Acid Concentration

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Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

Poly(aniline) was synthesized by electrochemical oxidation from phosphoric acid at concentrations from 0.1 mol/L up to 7 mol/L in an electrochemical quartz crystal microbalance (EQCM) equipped cell in a three-electrode configuration. Deposition processes were monitored by a recently introduced fast impedance-scanning quartz crystal microbalance to determine the optimal concentration for most effective electropolymerization parameters.

Keywords: Impedance scanning quartz crystal microbalance, EQCM, poly(aniline), electrodeposition, H₃PO₄

1. Introduction

At first introduced by Shirakawa et al.,¹ conducting polymers capture various fields of applications from that time on,² including conducting adhesives, electromagnetic shieldings, printed circuit boards (PCB's), antistatic coatings, electrical displays and organic light emitting diodes (OLEDs), chemical, thermal and biological sensors, ion exchange membranes, batteries, and for supporting of biomolecules. Many groups do research on these fields.

Basically there exist two main methods to polymerize the monomers, building the conducting polymers in situ. Either by addition of an oxidizer, such as APS (ammonium persulfate),^{3–6} or by electrochemistry.^{7,8}

In situ polymerization by electrochemistry may be the preferred way, because the reaction conditions involving oxidation of the monomer can be more rigorously controlled. Cyclic voltammetry (CV) is the method of choice, delivering maximum information content.

Tracking and investigating the deposition process, a couple of (partially in situ applicable) methods were established, such as scanning electron microscopy (SEM),⁹ transmission electron microscopy (TEM),¹⁰ Fourier trans-

form IR spectrometry (FTIR),^{11,12} Raman,¹³ UV-Vis,¹⁴ electron spin resonance (ESR),¹⁵ nuclear magnetic resonance (NMR),¹⁴ thermo gravimetric analysis (TGA),¹⁴ X-ray diffraction,¹³ X-ray photoelectron spectroscopy,¹⁶ mass spectrometry (MS)¹³ and electrochemical impedance spectrometry (EIS).¹⁷

Making use of quartz crystal microbalance (QCM)¹⁸ techniques Yang et al.¹⁹ apply an adapted impedance spectrum analyzer for monitoring electropolymerization and degradation procedures on the sensor crystal. This increases the extent of information²⁰ compared to traditional QCMs oscillator techniques, but has been shown not to be an appropriate method, if fast frequency changes have to be monitored.²¹ It was indicated to strike a balance between complexity and extent of information, so that a fast impedance scanning QCM method was developed.²² Common problems, such as combination of electrochemical methods with the QCM, combination of data without detouring over analogue inputs and outputs, heavy liquid damping levels, observation of many cycles in the CV experiment, and speed tasks have been solved.

To find the optimal conditions for the electropolymerization of aniline, the parameters: concentration of

phosphoric acid and the number of cycles are screened to deposit the polymer most effectively.

The simplified Sauerbrey equation has been used to determine the change in electrode mass Δm assuming deposition of a rigid and homogeneous film,²³

$$\Delta\nu = -C_f \Delta m$$

where $\Delta\nu$ is the frequency shift in Hz and C_f is the reduced sensitivity factor, typically expressed in items of Hz/ μg .

2. Experimental

2.1. Instrumentation

Electrochemical experiments are conducted using a standard three-electrode cell assembly – compare to Figure 1.

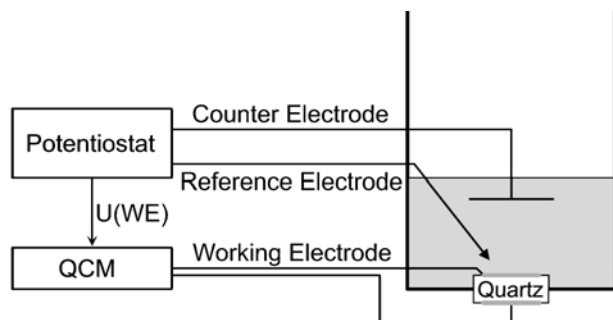


Figure 1: Simplified connection diagram forming an EQCM experiment.

A quartz crystal (MAXTEK SC-101, gold-surface, 6 MHz, 0.55 inch diameter, electrode area: 0.357 cm²) as mass-sensitive device is contained at the bottom of a glass-cell, sealed using an arrangement of a KEL-F molding and several joint-rings (Kalrez elastomer).

The top side of the sensor acts as working electrode, connected to the home-built precision potentiostat, respectively. The quartz crystal's bottom electrode is electrically connected to the impedance scanning QCM device. Previously we determined a sensitivity factor of 246 Hz/ μg at the series resonance frequency (ν_s)²² for this type of quartz crystal.

The counter electrode is a platinum sheet, the reference electrode an Ag/AgCl electrode from BAS (RE-5B) with a porous Vycor glass tip. All electrochemical potentials are given with respect to this electrode, unless stated otherwise.

2.2. Reagents

Aniline monomer (H₂NC₆H₅, Merck, Darmstadt) was freshly distilled (95 °C, 1 mbar) and stored at a dark

place in the refrigerator. Phosphoric acid (H₃PO₄, Merck, 85%, p.a.) was used as received. For preparation of the solutions, Milipore quality water was employed. Sulfuric acid (H₂SO₄, Merck, p.a.) and hydrogen peroxide (H₂O₂, Merck, medical grade) were used for activation and cleaning purposes.

2.3. Preparation

Several standard solutions containing 0.1 mol/L (M) aniline monomer with variable H₃PO₄ concentrations (0.10, 0.42, 0.50, 0.75, 1.50, 2.02, 3.22, 4.05, 5.00, 7.00 M \pm 0.01 M) were prepared by determining the components' masses.

Before a polymer-forming investigation is started, the cell is cleaned with water and H₂O₂, and a brand-new quartz crystal is activated. For that purpose the cell is filled with 0.1 M H₂SO₄, deaerated with purified nitrogen, and performing several anodic CV scans in the range 0.35–0.7 V until no more changes in the cyclic voltammogram (CV) can be recognized. Subsequently, after a further cleaning step, the cell is filled with one of the deaerated standard solutions. The hybrid EQCM experiment joining the CV and the QCM measurement is started, datasets containing voltage, current and resonance frequencies are obtained with full digital resolution, without detouring over analogue inputs and outputs, an advantage of this kind of setup.

The CV experiment is performed with a linear voltage sweep starting at –0.24 V in anodic direction at a sweep rate of 10 mV/s, and a second vertex potential of 0.9 V. Twenty cycles are gathered. The impedance scanning QCM experiment conducts data with a resolution of 0.5 Hz, the series resonance frequency is evaluated. The datasets are online-processed using a standard PC.

3. Results and Discussion

Figure 2 shows a typical cyclic voltammogram used for electropolymerization and a frequency evaluation curve as determined by a QCM measurement, giving information about the agglomerated mass.

The mechanism for the electrodeposition of aniline is well-known.^{7, 24, 25, 26} So that in Figure 2 the region marked as (I) shows the initiation process, building the radical cation of the monomer. The radical cation is stabilized by the mesomeric effect. Region (II) shows the chain propagation. This is in a good agreement with the effects that can be observed in the frequency evaluation curve on the top. Starting with 0 Hz the series resonance frequency (ν_s) decreases during these processes. At the end of the whole cycle a hysteresis of about 1200 Hz can be recognized. This hysteresis shows the irreversible deposition of poly(aniline) in this cycle and is hence called $\Delta\nu_{s, \text{end}}$. The maximal change in frequency ($\Delta\nu_{s, \text{max}}$) can be observed at

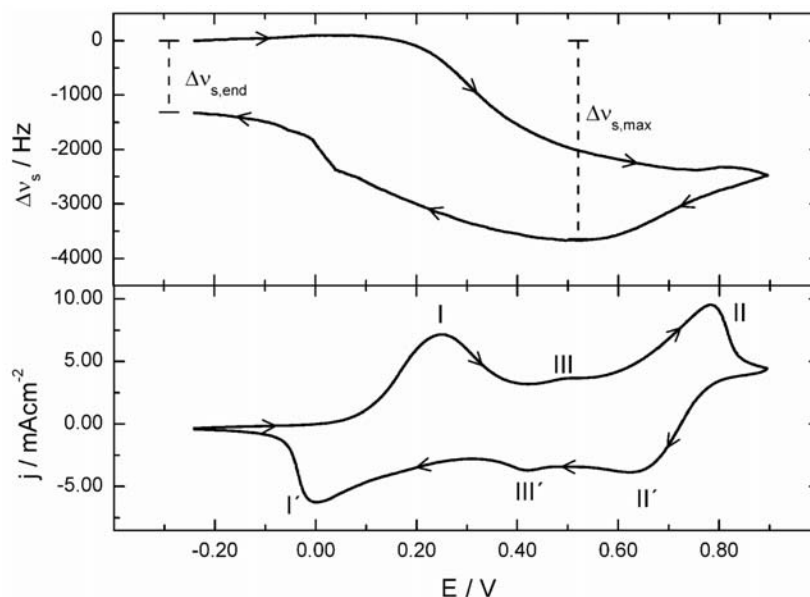


Figure 2: Frequency evaluation curve (top) and cyclic voltammogram (bottom) from 0.1 M aniline and 1.50 M H_3PO_4 , the 20th cycle is shown.

about 0.5 V. The slow rise in the current density in region (III) is excessively discussed in literature.^{7,27} Because of no related effect in the frequency evaluation curve this “middle peak” is of no significance for us. Under some circumstances it can happen that the polymer flakes off, this can be seen very illustratively at the step appearing at the end of the frequency 3rd and 4th curve at about 0 V.

Figure 3 shows a typical EQCM behavior of electropolymerization over four cycles.

The cyclic voltammogram shows a typical behavior of an autocatalytic process²⁸ with growing peak currents. It can be seen clearly, that the maximal change in fre-

quency ($\Delta v_{s,end}$) increases from cycle to cycle. This effect also holds true for $\Delta v_{s,max}$.

Figure 4 shows the so-called calibration curve. The change in frequency is drawn against the electric charge during the CV experiment. The regions I to III are linked to those in Figure 2.

Analyzing the frequency evaluation curves ($\Delta v_{s,end}$ as well as $\Delta v_{s,max}$) – with respect to acid concentration and cycle number – leads to the graphs shown in Figures 5 and 6 with more than 500 data points at all. This allows to make conclusions about the efficiency of the polymerization process.

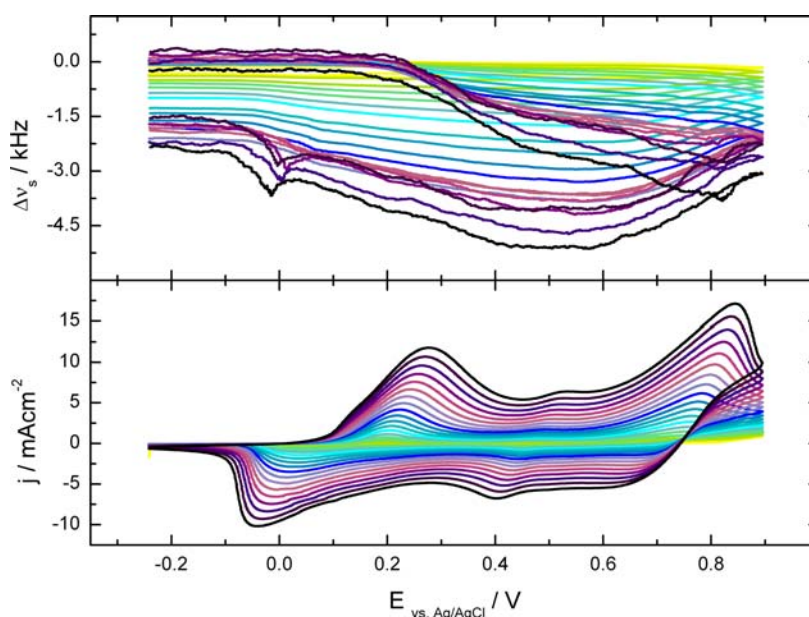


Figure 3: Frequency evaluation curves (top) and cyclic voltammograms (bottom) from 0.1 M aniline and 2.02 M H_3PO_4 are shown.

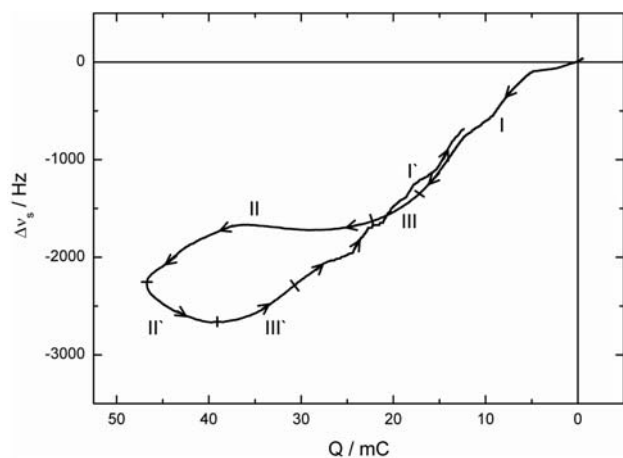


Figure 4: The calibration curve is shown, at a concentration of 0.75 M at the 20th cycle.

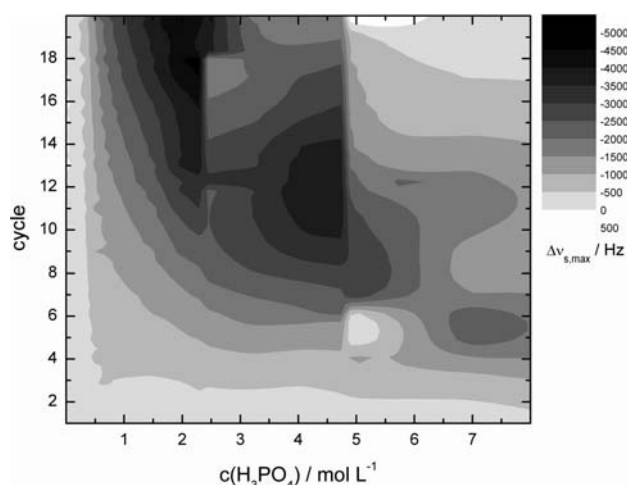


Figure 5: Evaluation of $\Delta v_{s,max}$ over up to 20 cycles in the CV experiment and at various concentrations of phosphoric acid.

It is obvious, that the overall maximum of mass deposition is located at 18 cycles in the CV and at a concentration of 2 M phosphoric acid with a change in frequency of more than 5000 Hz. At the concentration of 4 M a remarkable deposition even earlier at 12 cycles can be found with a change in frequency of about 3500 Hz. Durable deposited polymer over the whole CV process, shows the maximum deposition rate located at 12 cycles at an acid concentration of 4 M.

4. Conclusions

In general at a phosphoric acid concentration of 4 M and a number of 12 cycles, the best deposition rate can be found, with a minimum in mass-dispatch of the agglomerated polymer.

Upscaling for industrial processes, especially in corrosion-protecting application of large copper areas in pre-

sence of phosphoric acid is now possible with a high gain. The optimum that was found is obviously a compromise in the conductivity of the phosphoric acid and the increasing viscosity. The impedance scanning QCM showed to work perfectly even at high extents of damping and loading through the polymerized coat.

5. Acknowledgment

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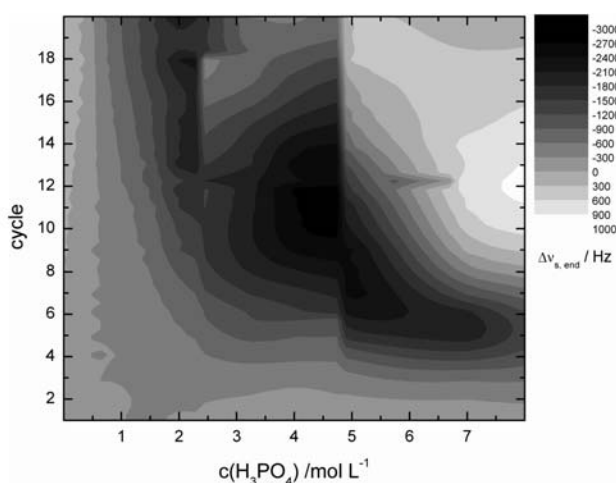


Figure 6: Evaluation of $\Delta v_{s,end}$ over up to 20 cycles in the CV experiment and at various concentrations of phosphoric acid.

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Povzetek

Z metodo elektrokemične oksidacije smo v elektrokemijski kvarčni mikrotehnikci s tremi elektrodami iz fosforne kisline različnih koncentracij ($c = 0.1 \text{ mol/L} - 7 \text{ mol/L}$) sintetizirali poli(anilin). Da bi določili optimalne pogoje elektropolimerizacije, smo proces spremljali s hitrim koračnim merjenjem impedance.