Characterization of Electrochemically Deposited Polypyrrole Using Magnetoelastic Material Transduction Elements

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Magnetoelastic alloy films have been used as a working electrode in an electrochemical cell. This material allows magnetic interrogation of electrochemical deposition. This technique was used to monitor the electrochemical deposition of polypyrrole by multisweep (CV) and potentiostatic methods. Since the determination of the mass-sensitive magnetoelastic film's resonance frequency is based on magnetic transduction, an inherent advantage of this method is that it requires no electrical connections other than the working lead of the potentiostat. Increases in pyrrole deposition correlated with a decrease in the peak resonance frequency of the magnetoelastic alloy. This technique provides a novel approach by which one can monitor electrochemical processes.

Magnetoelastic thick film transducers can be fashioned from a class of amorphous iron- and cobalt-based alloys.[1−4] These materials can be excited by an external AC magnetic field to produce longitudinal elastic standing waves at the films' mechanical resonance frequencies. The operation of these alloys is analogous to the functioning of surface acoustic wave (SAW) devices. In contrast to SAW devices, the interrogation of magnetostrictive materials can be performed via magnetic fields; therefore, no wired connections to the films are necessary to monitor the resonance frequencies of these materials. Relatively inexpensive to produce, these films are widely used in retail stores as disposable antishoplifting markers.[5]

The sensing properties of magnetoelastic materials enable the fabrication of a number of different types of sensors. Since changes to the surface of these material cause changes in their inherent response, they have been utilized as physical sensors. In this capacity, magnetoelastic alloys have been used to measure torsion,[6] temperature,[7,8] humidity,[7] pressure,[8] liquid density,[9] and viscosity.[9] Magnetoelastic materials have also been used in biomedical applications to measure strain in the healing of fractured bones,[10] and to measure muscle stresses in vivo.[11] The inclusion of chemically sensitive polymer surface coating on strips of magnetoelastic alloys have allowed development of chemical sensors. Published work of this type from the Grimes' research group includes demonstration of operational magnetoelastic-based pH,[12,13] ammonia,[14] and glucose sensors.[15]

The underlying mechanism that allows the type of magnetoelastic transducer described in this manuscript to work is the interrogation and detection via magnetic fields. A specific-frequency AC magnetic field is applied to the magnetoelastic alloy, which efficiently converts magnetic energy into elastic energy. This elastic energy causes deformation of the strip. This deformation is the greatest when the frequency of the AC magnetic field matches the strip's fundamental mechanical resonance frequency. The magnetoelastic strips also have the property of magnetostriction, which means that as the film undergoes deformation, it generates a magnetic flux. It is this magnetic flux that is also proportional to the deformation that is detected at the pickup coil as the sensor signal. A DC magnetic field is used to offset the strips' magnetic anisotropy, thus enhancing the magnetoelastic response of the strips.

Since the magnetoelastic films are metallic alloys and are conductive, it is reasonable to expect that these materials could function as working electrodes in an electrochemical cell. Additionally, as shown herein, the magnetoelastic strips can be coated with metal evaporated films without interfering with the resonance monitoring. Electrochemical experimentation can then be magnetically monitored using these strips. This technique is particularly useful in the investigation of electrochemical depositions.

Herein, we describe the first application of magnetoelastic transduction to monitor electrochemical events in conjunction with the electropolymerization of the conducting polymer, polypyrrole. To avoid confusion, it should be noted that in this work, the

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magnetic fields are *not* used to facilitate/control the electropolymerization. Thus, the magnetohydrodynamic (MHD) force, which is the principle result of applying magnetic fields to electrolyte solutions, is not operative during our experiments; for examples of published work dealing with MHD and electrochemistry, see refs 16−22.

The in situ monitoring of electrochemical conducting polymer film growth has been previously performed by optical methods, such as spectroscopic elipsometry,[23,24] FT-IR,[24] and XPS.[25] Polypyrrole growth has been studied extensively by the use of electrochemical quartz crystal microbalances (EQCM); for examples, see refs 26−31. A drawback of using EQCM to monitor electrochemical polymerization is the number of connections made from the potentiostat and oscillator circuitry to the crystal and the need to isolate these systems from each other. With the magnetoelastic transduction described, the only connection to be made is from the strip of film to the potentiostat. The change of peak resonance frequency response due to the electrochemical deposition of polypyrrole onto a magnetoelastic film can be monitored, thus providing another dimension of analysis for electrochemical processes.

EXPERIMENTAL SECTION

Materials. Hexaamineruthenium (III) chloride ($Ru(NH_3)_6Cl_3$) was purchased from Alfa Aesar (Ward Hill, MA). A solution of 5.0 mM $Ru(NH_3)_6Cl_3$ was prepared using distilled, deionized water (Milli-Q water purification system, Millipore, Bedford, MA) and contained 0.10 M potassium chloride (Fisher Scientific, Fair Lawn, NJ). Pyrrole (Py) received from Sigma (St. Louis, MO) was distilled in an inert atmosphere and stored in the dark at 4 °C. Tetraethylammonium-*p*-toluenesulfonate (TEATS) and propylene carbonate were obtained from Aldrich (Milwaukee, WI). Solutions of 0.10 M Py in propylene carbonate with 0.10 M TEATS used as the supporting electrolyte were prepared for the electrochemical deposition on the working electrode. Magnetoelastic strips of Metglas 2826MB, which have a composition of $Fe_{40}Ni_{38}Mo_4B_{18}$ (Honeywell, Parsippany, NJ), were used as the working electrode/magnetoelastic transducer in this work. The size of the strips was typically in the range of 50.8−63.5 mm in length, and is 6.5 mm wide and 30 μm thick, with the fundamental resonance frequency of the sensor being proportional to its length. A Ag/AgCl microelectrode (model RE-5B, Bioanalytical Systems, West Lafayette, IN) and a Pt wire were used as the reference and counter electrodes, respectively.

Methods. Gold was evaporated onto some of the magnetoelastic strips from a 99.99% gold wire (Spectrum, New Brunswick, NJ). Roughly 400 nm of gold was coated onto each side of a strip before it was used in polymerization studies. An EG&G PAR model 273 potentiostat was used to perform the electrochemical experiments. Cyclic voltammetry of $Ru(NH_3)_6Cl_3$ was performed by cycling the potential from +0.1 to −0.4 V at 100 mV/s. Polypyrrole was formed onto the magnetoelastic working electrode by repetitive cycling of the potential from +1.2 to −0.8 V at 100 mV/s for up to 40 cycles. Pyrrole deposition onto the magnetoelastic material was also performed using a potentiostatic method, with a polymerization potential held at +0.95 V.

The resonance frequency measurements were made using a setup previously described.[32] Briefly, both a 5.0 Oe DC magnetic field to offset the strips' magnetic anisotropy and a 50 mOe sinusoidal AC magnetic field for interrogation of the transducer were generated by coils in the Helmholtz configuration. A pickup coil was used to monitor the change of magnetic flux caused by the resonance frequency changes in the magnetoelastic films. The pickup coil signal was fed into a low-noise preamplifier and a lock-in amplifier before data acquisition by a computer. The computer also controlled the application of the DC and AC magnetic fields. The resonance frequency of the sensor can be readily measured to an accuracy of 0.25 Hz. The magnetoelastic films had a connector pin soldered to their center, the vibration null point of the characteristic resonance frequency, as a contact for the potentiostat lead. Null point connections have been used successfully to keep from completely dampening the magnetoelastic resonance response in other work.[32] After a particular number of voltammetric cycles during the deposition of the polypyrrole film, the peak resonance frequency of the working magnetoelastic electrode was determined by scanning the AC magnetic field with the largest amplitude determining the resonance frequency. In a separate experiment, the peak resonance frequency was monitored after certain periods of potentiostatic electrochemical polymerization of pyrrole onto a magnetoelastic working electrode. *The potentials were not applied during any resonance frequency measurements.* The experimental setup is depicted in Figure 1. The magnetoelastic strips are placed between the pickup coils for measurements.

RESULTS AND DISCUSSION

The cyclic voltammogram (CV) of hexaamineruthenium (III) chloride demonstrated, when used bare, the magnetoelastic alloy is not a "well-behaved" electrode material. However, when using a magnetoelastic working electrode coated in evaporated gold, anodic and cathodic peaks become clearly visible in the CV of hexaamineruthenium (III) chloride. Coating the magnetoelastic strips by evaporating gold onto their surface allows faradic reactions involving electrochemically active species to occur. This characteristic provides the opportunity to monitor the results of electrochemical processes by magnetic interrogation. Both uncoated and gold-coated magnetoelastic strips were used in the

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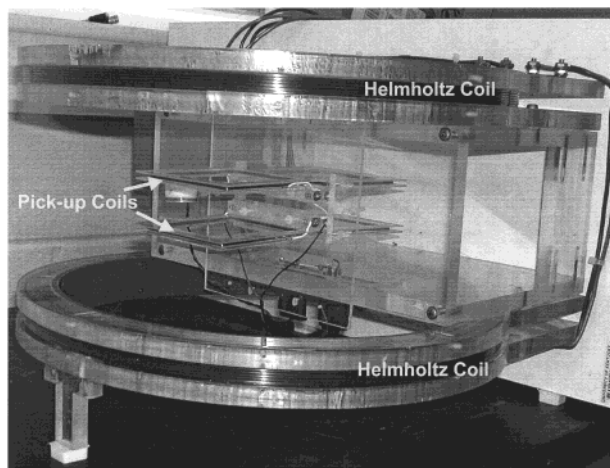
Figure 1. Picture depicting the experimental setup for the magnetoelastic monitoring of electrochemically deposited polypyrrole.
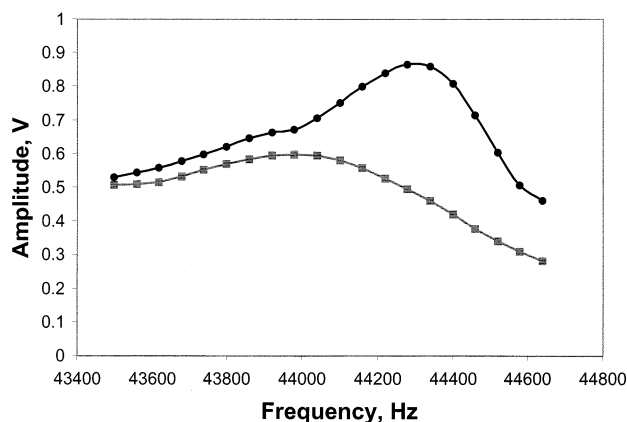

Figure 2. Magnetoelastic resonance frequency scans of a magnetoelastic film electrode before pyrrole polymerization (circles) and after 40 voltammetry cycles (squares).

Figure 3. Magnetically interrogated peak resonance frequency as a function of potential cycles used to electropolymerize pyrrole onto the magnetoelastic working electrode. Lettering refers to the voltammograms shown in Figure 4.

Figure 4. Cyclic voltammograms of deposited polypyrrole after (A) 1 cycle, (B) 5 cycles, and (C) 40 cycles.

monitoring of electrochemical polymerization of pyrrole. The results for both types of strips are discussed below.

Magnetic Monitoring of Cyclic Voltammetric Polypyrrole Formation Using Uncoated Magnetoelastic Strips. The measured frequency spectrum of an uncoated magnetoelastic strip and the same strip after 40 cycles for polymerization of pyrrole can be seen in Figure 2. As seen in this figure, the peak resonance frequency of the magnetoelastic film decreases with the applied polymer mass load. The amplitude of the response for the sensor coated with the electrodeposited polymer is lowered as a result of a reduction of the surface vibrational amplitude.

The resonance frequency as a function of the number of voltammetric cycles involved in polypyrrole formation is shown in Figure 3. After a particular number of cycles, the peak resonance frequency was determined by magnetic interrogation. During the first several redox cycles, the resonance frequency peak changes linearly to lower frequencies. After 10 potential cycles, the resonance peak continues to decrease in frequency, but at a lower rate. The corresponding cyclic voltammograms (CVs) of the pyrrole film formation are displayed in Figure 4. The lettering of certain positions in Figure 3 corresponds to the CVs shown in Figure 4 (i.e., A corresponds to the first cycle, B corresponds to the fifth cycle, and C corresponds to the fortieth cycle). After the first potential cycle, the oxidative peak can be
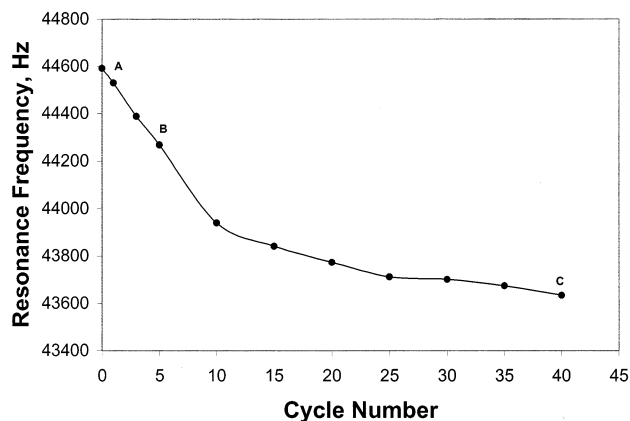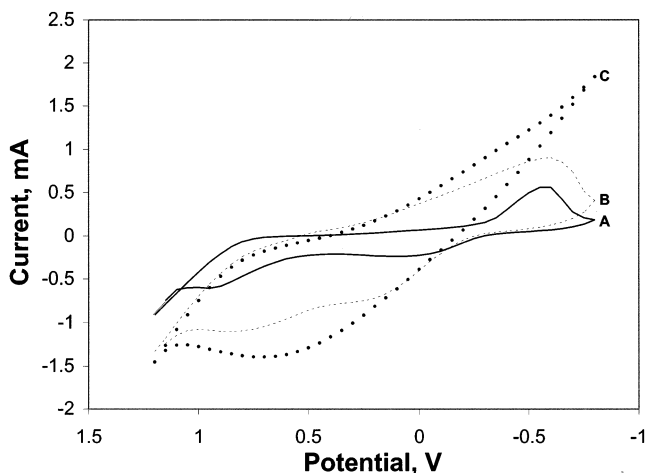
seen to greatly increase in current on subsequent scans. Note: as the overall current increases (i.e., as more polypyrrole is deposited), there is a decreasing shift of the peak resonance frequency.

Magnetic Monitoring of Potentiostatic Polypyrrole Formation on Gold-Coated Magnetoelastic Strips. The amount of pyrrole deposited over time during polymerization in a potentiostatic mode onto a gold-coated magnetoelastic strip was monitored. The secondary resonance peaks seen in Figure 5 are most likely due to the changing of the boundary conditions of the resonance by the attachment of the connection pin. The total charge passed over a certain period of time can be used to calculate the mass of the polypyrrole deposited onto the magnetoelastic working electrode. The peak resonance frequency was also obtained at various times during the electropolymerization.

Sauerbrey originally described the surface mass load-frequency relationship for thickness-shear mode quartz crystals.[33] However, this equation has also been used to describe the response of other types of sensors (e.g., magnetic-acoustic-resonator sensors[34,35])

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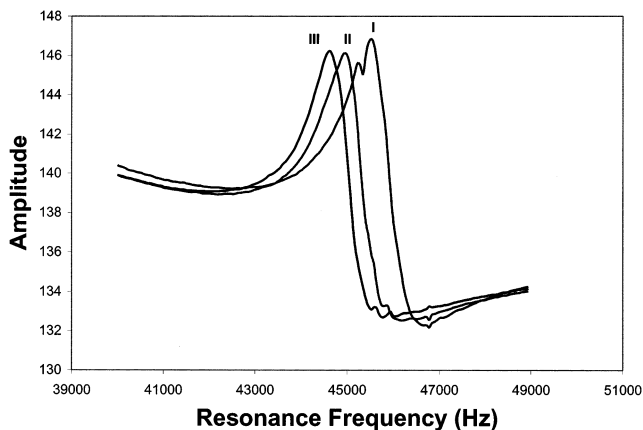
Figure 5. Magnetoelastic resonance frequency spectra collected after potentiostatic polypyrrole formation onto the magnetoelastic strip. The deposition potential was +0.95 V versus Ag/AgCl reference. Spectra shown were obtained after polymerization times of (I) 0, (II) 30, and (III) 45 min.

that behave in a similar fashion as do QCM. For small mass loads, the change in peak resonance frequency of the magnetoelastic film is described by the Sauerbrey expression in the form[36]

$$\Delta f = -f_0 \frac{\Delta m}{d_s t_s A}$$

where Δf is the resonance frequency shift in Hz, f_0 is the fundamental magnetoelastic sensor resonance frequency in Hz, Δm is the mass loaded onto the film (g), d_s is the density of Metglas 2826B (7.9 g cm^{-3}), t_s is the thickness of the magnetoelastic strip (30 μm), and A is the surface area of the sensor in which material is deposited (cm^2). The theoretical frequency shift was determined on the basis of the fundamental, unloaded sensor peak resonance frequency (f_0) for deposited masses. In Figure 6, the continuous predicted response of resonance frequency shift of a given gold-coated magnetoelastic strip versus the mass deposited onto the strip based on the equation above is shown as a solid line. The experimentally obtained shifts of the peak resonance frequency measured after periodical deposition of electropolymerized pyrrole versus the calculated polypyrrole-deposited mass obtained by measurements of the charge passed are also given in the figure as individual data points. The equation above holds true only when the mass load is very small relative to the mass of the sensing strip. The deviation of the last experimental point shown in Figure 6 from the theoretical response is due to the relatively high mass deposited compared within the useful limit of the above equation. The mass of the pyrrole at this point in the experiment is ~1% of the mass of the magnetoelastic strip. Use of larger strips should allow for an increase in the upper limit of mass for which this system could be used.

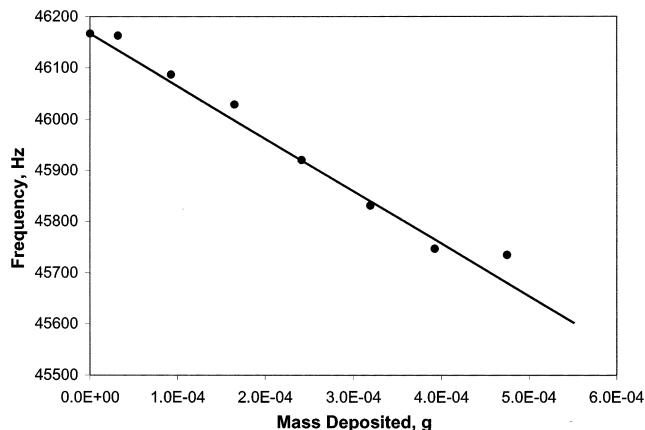(36) Rodahl, M.; Kasemo, B. *Sens. Actuators A* **1996**, *54*, 448−456.

Figure 6. Peak resonance frequency as a function of electropolymerized polypyrrole potentiostatic deposited onto a magnetoelastic electrode (circles) and the calculated theoretical response (line).

The magnetoelastic alloys operate in a fashion similar to EQCM devices. Using the example of thin films in liquid media being detected with a 5 MHz fundamental frequency QCM[31] and detection of an even coating onto the surface of a magnetoelastic strip,[7] some comparisons of the detectable mass limit and sensitivity can be made. The mass detectable by the QCM is ~3.5 orders of magnitude lower than that of the magnetoelastic material. The magnetoelastic film, however, is ~1.5 orders of magnitude more sensitive than the QCM.

CONCLUSION

In conclusion, magnetoelastic alloy film can be used as an electrochemical-working electrode. Coating the magnetoelastic strips with a film of evaporated gold improves the electrochemical properties while not causing interference for the peak resonance frequency measurements. The ability to simultaneously perform electropolymerization of pyrrole and then interrogate the system by magnetoelastic transduction is a new monitoring method for investigating electrochemical depositions. The overall trend that was observed with the formation of polypyrrole onto the magnetoelastic working electrode is a decrease in the peak resonance frequency. The research presented shows the feasibility of magnetic-interrogation of other electrochemical processes.