A wireless micro-sensor for simultaneous measurement of pH, temperature, and pressure

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Abstract
In response to a magnetic field impulse, magnetostrictive magnetoelastic
sensors mechanically vibrate. These vibrations can be detected in several
ways: optically from the amplitude modulation of a reflected laser beam,
acoustically using a microphone or hydrophone, and by using a pickup coil
to detect the magnetic flux emitted from the sensor. Earlier work has shown
that the resonant frequency of a magnetoelastic sensor shifts in response to
different environmental parameters, including temperature, pressure, fluid
flow velocity and mass loading, with each parameter determined in an
otherwise constant environment. To extend the utility of the sensor
technology in this work we report on the fabrication and application of a
miniaturized array of four magnetoelastic sensors that enable the
simultaneous remote query measurement of pH, temperature, and pressure
from a passive, wireless platform.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

1. Introduction

Surface acoustic waves and piezoelectric microsensors are
widely used for measuring changes in temperature, pressure,
viscosity, and density of a medium in contact with the sensor
surface [1–3]. These devices require electrical connections
between the sensors and the detection electronics, a constraint
that precludes many *in situ* and *in vivo* monitoring applications.

One way to overcome the constraint of needing electrical
connections with the sensors is to use a magnetoelastic, rather
than piezoelectric, substrate. Magnetostrictive magnetoelastic
thick-film sensors mechanically deform when subjected to
a magnetic field impulse, launching elastic waves within
the sensor the magnitude of which are greatest at the
mechanical resonant frequency of the sensor. The mechanical
deformations of the sensor launch magnetic flux that can be
detected remotely by a pickup coil [4], and are of sufficient
amplitude to enable acoustic monitoring [5] over a range
of meters.   Furthermore, the sensors can be monitored
optically through the amplitude modulation of a laser beam
reflected from the surface of the sensor. A schematic drawing
illustrating the remote query nature of the sensor platform is

shown in figure 1. In response to a magnetic field impulse
the sensor vibrates; the magnetic, acoustic or optical time-
amplitude response is captured, and converted to frequency-
amplitude using a FFT algorithm from which the resonant
frequency of the sensor is readily determined.

The characteristic, longitudinal resonant frequency of a
ribbon-shaped unloaded magnetoelastic sensor in air is given
by [6]:

$$f_0 = \sqrt{\frac{E}{\rho(1-\sigma^2)}}\frac{1}{2L}.\tag{1}$$

The resonant frequency is a function of sensor length L, as
well as the density ρ, elasticity E and Poisson's ratio σ of the
sensor material.

Earlier work has shown that the resonant frequency of a
magnetoelastic sensor changes in response to temperature [4],
pressure [4], ambient flow rate [7], and liquid viscosity and
density [8]. Mass loading also shifts the resonant frequency
of the sensor, hence passive, wireless chemical sensors can
be fabricated by combining magnetoelastic sensors with
chemically responsive, mass changing layers. However, since
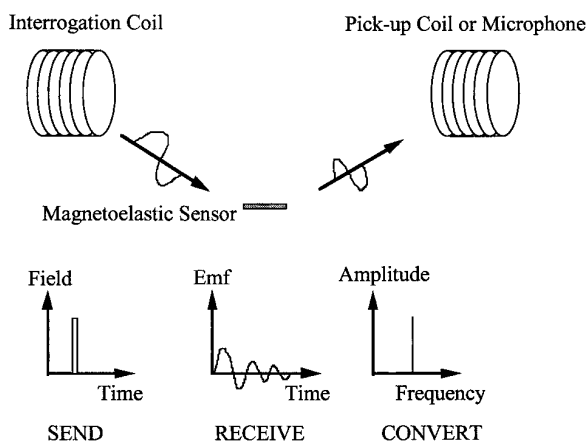magnetoelastic sensors respond to the different environmental

Figure 1. Schematic drawing illustrating the remote query nature of the passive, wireless sensor platform.

parameters in a non-separable fashion, earlier measurements required a fixed background while one parameter was varied. Further utility of the sensor technology requires methods that enable the simultaneous measurement of multiple environmental parameters, which is the topic of this paper.

2. Experimental details

In the present work we have fabricated a miniaturized array of four magnetoelastic sensors, of lengths 2.76, 2.71, 2.66, and 2.56 mm, each with an approximate aspect ratio of 7 and a thickness of 25 μm. The sensor array is shown in figure 2; the four sensors, laser cut from a continuous ribbon, are of slightly different lengths so that the operational range of their characteristic resonant frequencies do not overlap. The sensors are mounted on a micro-machined PC board using a thin layer of polyurethane adhesive, supported in cantilever fashion at their centers, the null point of the fundamental vibration mode.

Three sensors of the array are comprised of Metglas[1] alloy 2826MB ($Fe_{40}Ni_{38}Mo_4B_{18}$), and one sensor is made of Metglas alloy 2605SC ($Fe_{81}B_{13.5}Si_{3.5}C_2$). The two Metglas alloys have different elasticity–temperature responses [10], therefore comparison between similarly stressed sensors of each alloy enables an absolute determination of temperature although, for example, the ambient pressure to which both sensors are exposed may be changing. Recent work [11] has reported on how the pressure sensitivity of a magnetoelastic sensor can be tailored by stressing the sensor in a controlled fashion, either through in-elastic dimpling of the sensor or elastically bending it. The inherent stress causes the sensor to vibrate out-of-plane, with the relatively large ($\approx 10^{-6}$ m^2) basal-plane area of the sensor effectively coupling to the ambient atmosphere like a vibrating drum; the energy loss to the out-of-plane vibrations acts as a damping force to the mechanically resonating sensor. Higher stress levels in magnetoelastic sensors lead to greater frequency–pressure response slopes. In the unstressed sensor the vibrations are almost exclusively longitudinal. Since the surface area of the longitudinal ends of the sensor are negligibly small, less than 10^{-9} m^2, ambient pressure has almost no affect

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[1] The Metglas alloys are a registered trademark of Honeywell Corporation. For product information, see the web page [9].

on a longitudinally vibrating sensor [11]. Therefore, in the array there is a stressed 2826MB alloy sensor, non-elastically dimpled by application of mechanical punch, which has a significantly higher frequency–pressure response (0.04% shift in resonant frequency/psi) than the unstressed sensor the frequency response of which is virtually constant with pressure. Comparison between the stressed and unstressed 2826MB sensors enables an absolute pressure measurement in a changing temperature environment.

Coating a sensor, i.e. applying a mass load, changes the characteristic resonant frequency f_0. For small mass loads, as the mass load increases the resonant frequency linearly shifts lower with the change in the resonant frequency given by [4]:

$$\Delta f = f - f_0 = -f_0 \frac{\Delta m}{2M} < 0. \qquad (2)$$

With reference to equation (2) passive, wireless chemical sensors can be made by combining the magnetoelastic sensor with a mass changing, chemically responsive layer.

The wireless, remote query nature of the sensor technology makes it ideally suited for monitoring the environmental conditions from inside sealed, opaque containers—such as people. One potential application of this sensor technology is in the monitoring of gastric pH from a small, disposable pill-like sensor for the diagnosis of gastroesophageal reflux disease (GERD) [12–15]. GERD is a disorder related to the retrograde movement of gastric acid into the esophagus from the stomach, the physiological condition of which is related to inadequate resting tone or relaxation of the lower esophageal sphincter [12]. GERD is among the most common digestive problems in the United States, with 4–7% of the population experiencing symptoms such as severe heartburn daily [14, 15]. To establish a diagnosis of GERD, current practice requires a catheter to be placed trans-nasally in the patient, which measures pH over a 24-h period [16–20].

As the remote query magnetoelastic micro-sensor array is small enough to be easily swallowed, readily monitored over several tens of centimeters, and has a small enough unit material cost to enable use on a disposable basis, the technology appears ideally suited for simultaneous monitoring of gastric pH, temperature, and pressure. A patient undergoing testing would have only to swallow a pill containing the micro-sensor array, which could then be monitored from a pickup coil embedded within a vest-like garment. Therefore, the fourth sensor in the micro-sensor array is coated with a pH responsive, mass-changing polymer, the fabrication and properties of which are described in the following section.

2.1. pH sensor fabrication

The pH responsive copolymer, poly(acrylic acid-co-isooctyl-acrylate), was synthesized at 70 °C by free radical copolymerization of acrylic acid and isooctylacrylate with an initial mole ratio of acrylic acid to isooctylacrylate of 1:1, and coated upon an unstressed flat 2826MB alloy sensor. In agreement with the work of Philippova [21], who described a similar polymer comprised of acrylic acid and an alkyl acrylate, the pH sensitivity of the polymer was increased with a higher acrylic acid fraction. In a 50 ml three-necked flask equipped with thermometer, magnetic stir, condenser, and
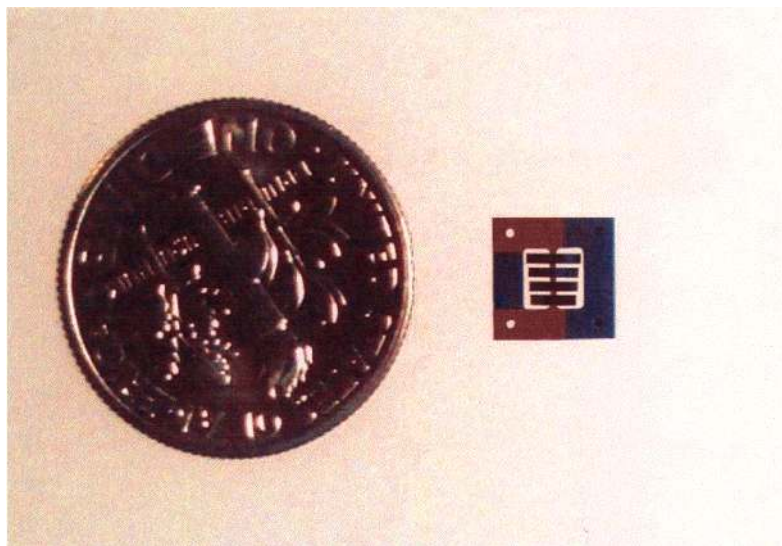
Figure 2. Optical image of the magnetoelastic micro-sensor array, with sensor elements cantilevered across a supporting micro-milled PC board. A US dime is shown for scale reference.

gas inlet was added 3.2 ml of acrylic acid and 10.5 ml of isoocylacrylate. The solution was deoxygenated by bubbling nitrogen through the solution for an hour while stirring. Then 0.08 g (0.5 mol%) of 2,2′-azobis(isobutyronitrile) was added as initiator. The temperature was slowly raised to $70\,°C$ to start the polymerization, and maintained at $70\,°C$ for 3 h to complete the polymerization in a nitrogen atmosphere. The prepared copolymer was washed with hexane thoroughly to remove the unreacted components and dried in a vacuum oven at $120\,°C$ under reduced pressure (<20 Torr) overnight. The resulting polymer density was 1.04 g ml^{-1}. (The acrylic acid and isooctylacrylate were purchased from Aldrich [22] and distilled under reduced pressure prior to use to remove the inhibitor, monomethyl ether hydroquinone. 2,2′-azobis(isobutyronitrile), ethanol, ethyl ether, and n-hexane were purchased from Aldrich, and polyurethane from Valspar Corporation [23], and used as received.)

Prior to coating, the magnetoelastic sensors were washed using cleaning solution[2] in an ultrasonic cleaner for 5 min, rinsed with water and acetone, and then dried with a stream of nitrogen. Prior to coating with the pH responsive polymer, polyurethane was applied on both sides of the sensor by dip-coating in $≈0.5$ wt% acetone solution; the resulting polyurethane layer was 0.4 μg. The polyurethane-coated sensor was then baked at $80\,°C$ for 4 h to form a durable and moisture resistant film that protects the sensor from rusting and also serves as an adhesion promoter between the metallic sensor and polymer. The polyurethane film is stable in alcohol, hexane, ether, and acetone; it can be removed by immersion in dimethylformamide for 5 min. The pH responsive polymer was then applied by dip-coating the 2.56 mm long sensor in a 1:1 ethanol and ethyl ether mixture solution at the concentration of 5 wt%. The polymer-coated sensors were dried in a vacuum oven at $80\,°C$ under reduced pressure (<10 Torr) overnight to remove the solvent. Microscope examination of the films indicated that relatively smooth, uniform films were obtained.

[2] International Products Co., PO Box 70, Burlington, NJ 08016-0070, USA (Cat No 6731).

Upon immersion in a liquid, as dependent upon solution pH, the polymer swells due to the electrostatic repulsion between charged groups, ion hydration, and the osmotic pressure exerted by mobile counterions [24]. Two counteracting forces determine the degree of swelling in an aqueous medium: the hydrophilic force due to the ionization and the attractive hydrophobic forces between alkyl groups. The carboxy group dissociates with increasing alkalinity, resulting in polymer swelling that increases the mass load on the sensor, thereby lowering the resonant frequency of the magnetoelastic sensor. A polymer thickness of approximately 0.7 μm was used, providing an experimentally determined optimum combination of rapid response time and sensitivity.

3. Experimental results

An 8 μs, 43 mOe magnetic field impulse was used to query the sensor array. The sensor array was monitored using a 10-turn, 20 cm diameter pickup coil located 15 cm away from the sensors. A 25 Oe dc magnetic field was applied along the length of the magnetoelastic sensors, by adjacent placement of a magnetically hard ferrite strip on the cantilever support structure, to enhance the longitudinal vibrations of the sensors [25–28]. The output of the pickup coil was initially passed through a SRS 560 [29] low noise pre-amplifier. From the pre-amplifier the time–amplitude response of the four sensors is captured using a HP 54810A oscilloscope, and converted to frequency–amplitude using a FFT algorithm within the oscilloscope, with a total data capture and analyses time of approximately 35 ms. The simultaneously measured frequency response of the four sensors, in air at room temperature, is shown in figure 3. The observed peaks are $≈30$ dB higher than the background noise level.

The micro-sensor array was placed within a chamber, the pressure and temperature of which could be independently adjusted; the chamber walls were made of non-conducting ceramic to avoid signal loss due to eddy currents. Figure 4 shows the normalized resonant frequency of a flat, unstressed
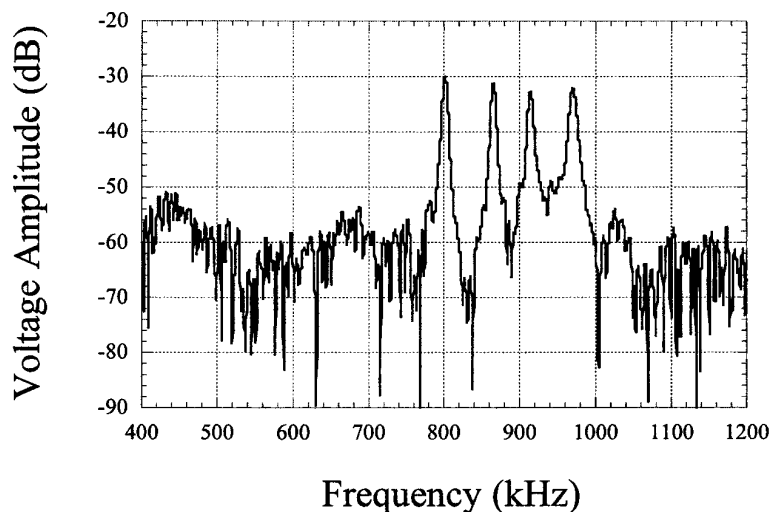
Figure 3. Measured frequency response, after FFT conversion, from the micro-sensor array shown in figure 2.
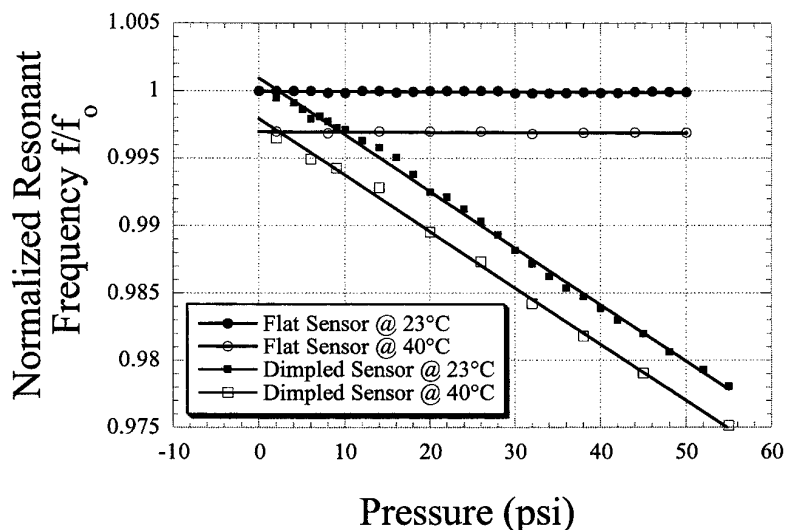

Figure 4. The normalized resonant frequency of an unstressed flat 2826MB alloy sensor, and a stressed (mechanically dimpled) 2826MB sensor, as a function of pressure at two different temperatures.

2826MB alloy sensor, and the otherwise identical sensor in which a dimple had been formed, versus pressure for two temperatures. The frequency–pressure responses of each sensor are normalized to their starting values measured at 1 atm pressure and room temperature; normalized frequency values are plotted as the two sensors have different characteristic resonant frequencies. As can be seen, comparison between the two sensors enables an absolute determination of pressure in a changing temperature environment.

Figure 5 shows the normalized resonant frequency of 2826MB and 2605SC alloy sensors versus temperature for two different pressures. The 2605SC alloy has a higher temperature coefficient of elasticity than the 2826MB alloy, and therefore a greater frequency versus temperature slope. The two sensors were elastically stressed by introducing a slight curve into the sensors, radius of curvature ≈100 mm, to introduce a small pressure dependence. Hence there is a small downward shift in the measured temperature–frequency responses of the two sensors. However, increasing pressure has the same effect on both similarly-curved sensors, therefore comparison between

the two sensors enables an absolute temperature measurement in a changing pressure environment.

3.1. Calibration and performance of pH sensor

The four-element sensor array, including the pH sensor comprised of an unstressed 2826MB element coated with the pH responsive polymer, was immersed in the middle of a plastic test cell (petri dish) that was placed within the temperature/pressure chamber. Immersing the sensor array within an inviscid liquid uniformly decreases the resonance frequency of each sensor by approximately 0.09%, consequently for precise measurements it is necessary to know if the sensor is in air or liquid. It should be noted that the support structure of the sensor array protects the sensor elements from unwanted interference such as, for example, pressure fluctuations forcing the sensors against the side of the chamber wall leading to spurious measurements.

Prior to pH testing, the sensor array was immersed in a neutral pH 0.1 mol l^{-1} KCl solution for 1 h to transform the
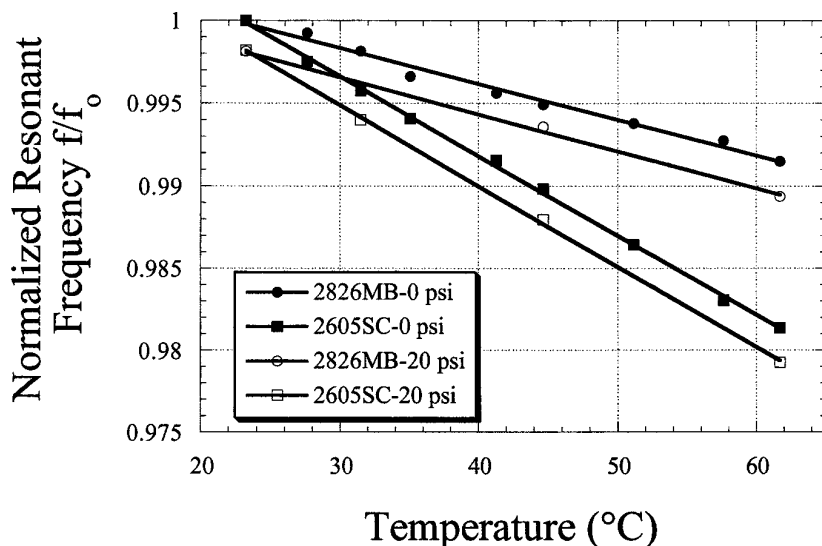
Figure 5. The normalized resonant frequency of a 2826MB alloy sensor, and a 2605SC alloy sensor, as a function of temperature at two different pressures. Both sensors are slightly curved, and hence demonstrate a similar, modest change in frequency with pressure.
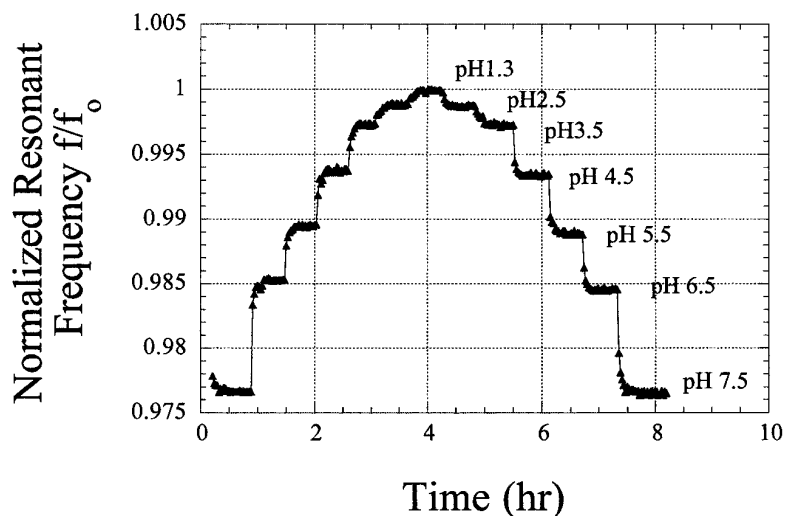

Figure 6. The calibration curve for the pH sensor. The frequency response is normalized to the measured value at pH 1.3.

pH responsive polymer from dry to wet state. The sensor array was then placed within a test solution of known pH and temperature, and the frequency spectrum of the array measured versus time. After each measurement the sensor and test cell were rinsed with de-ionized water, and the new test solution then added. The pH sensor was tested in solutions ranging from pH 1.3 to 7.5, which covers the range of pH values seen in gastric fluid [12, 13]. The pH sample solutions were made from a mixture of 0.05 mol l^{-1} acetic acid and 0.05 mol l^{-1} K$_2$HPO$_4$; the pH values were adjusted using 1 mol l^{-1} HCl or 1 mol l^{-1} NaOH and calibrated with a commercial pH meter (Orion 410A). The calibration curve, for a polymer thickness layer of 0.7 μm measured at 23.1 °C, is shown in figure 6. Figure 7 shows the response profile of the same sensor with pH decreasing from 7.5 to 1.3, and then increasing back to pH 7.5; the sensor was immersed in solution at each pH value for 4 min, measured, then moved to the next solution. The pH sensor shows greatest sensitivity between pH 4 and 7.5, with a resonant frequency shift of approximately 0.6%/pH. The

pH sensitivity of the copolymer was greatly enhanced by the relatively high concentrations of acrylic acid, allowing thinner films to be used with rapid response times: the response time to reach 90% of the steady-state value is less than 3 min for a 0.7 μm thick polymer layer.

Increasing temperature lowered the resonant frequency of the pH sensor more rapidly than that of the bare 2826MB sensor indicating, see equation (1), that the elasticity of the polymer film is decreasing with temperature more rapidly than the magnetoelastic amorphous metallic glass. This effect was linear for all pH values, and could therefore be accounted for by an initial calibration of the pH sensor response as a function of temperature. In contrast, it was found that pressure values up to 50 psi did not appreciably affect the pH measurements.

Figure 8 shows the response profile of a pH sensor as it is repeatedly cycled between pH 7.5 and 2.0. The change in the polymer mass between high and low cycles was approximately 0.18 μg, corresponding to a mass load differential of $\approx$50 ng mm^{-2} on each side of the sensor.
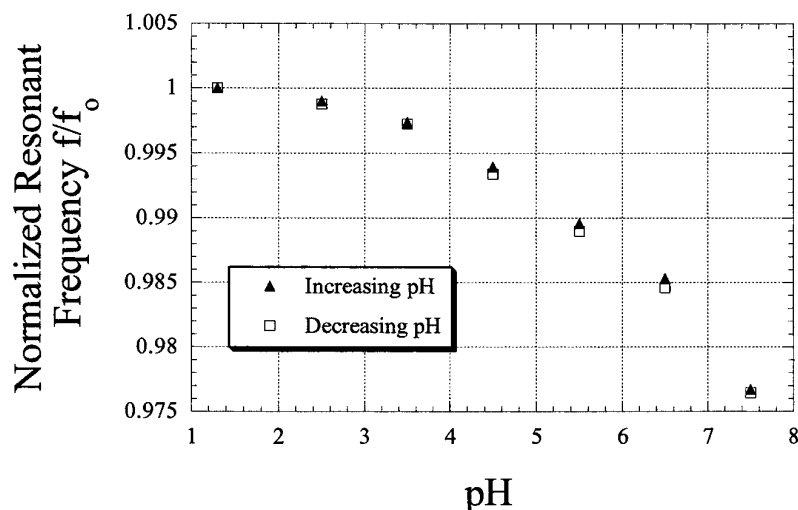
Figure 7. The normalized resonant frequency of the pH sensor for increasing and then decreasing pH levels. The response between pH 4 and 7.5 is approximately linear, with resonant frequency shift approximately 0.6%/pH.
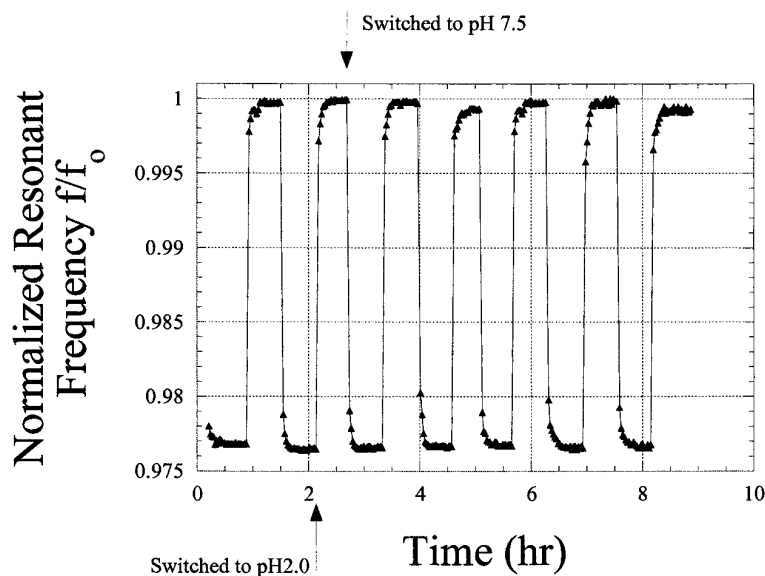

Figure 8. The normalized resonant frequency of the pH sensor as the solution pH is alternated between 2.0 and 7.5. The high/low mass change of the polymer layer is approximately 0.18 μg, corresponding to a mass differential of $\approx$50 ng mm^{-2} on each side of the sensor.

The measured values were highly reproducible, with a relative standard deviation over seven high/low pH cycles of 1.3%

4. Discussion and conclusions

A miniaturized four-element magnetoelastic sensor array has been described. The sensor array includes two similarly stressed 2826MB and 2605SC Metglas [9] alloy sensors, and a highly stressed inelastically dimpled 2826MB alloy sensor. Comparison between two similar sensors of different alloy composition enables an absolute temperature measurement in a changing pressure environment. In a similar fashion comparison between stressed and unstressed sensors of the same alloy enables an absolute pressure measurement in a changing temperature environment.

The fourth sensor in the described array is an unstressed 2826MB alloy sensor coated with a pH responsive, mass-changing polymer approximately 0.7 μm thick. The pH responsive copolymer, poly(acrylic acid-co-isooctylacrylate), was synthesized by copolymerization of acrylic acid and isooctylacrylate with an initial mole ratio of acrylic acid to isooctylacrylate of 1:1. The pH sensor is robust, operating over a 1.3–7.5 pH range, independently of pressure (to 50 psi), and temperature after an initial calibration.

The sensor platform is passive, with the sensors responding to the interrogation field consisting of an 8 μs 43 mOe magnetic field impulse. The sensor platform is wireless, with the sensor information, i.e. magnetic flux emitted by the vibrating magnetostrictive sensors, detected through the use of a remotely located pickup coil. The wireless, remote query nature of the sensor platform provides measurement of physical and chemical quantities without physical connections between sensor and detecting electronics. Furthermore, using a dynamic amplifier the sensors can be

monitored at almost any orientation with respect to the pickup coil, with the exception being when the basal plane of the sensor is parallel to that of the pickup coil.

The sensor array is small enough to be easily swallowed by humans, has a material cost low enough to be used on a disposable basis, and the described pH sensor successfully monitors the usual range of gastric pH values of 1.5–7.5 [12, 13]. Hence, the wireless sensor platform might find utility in the monitoring of gastric pH for diagnosis of gastroesophageal reflux disease [14, 15], avoiding the currently used trans-nasally placed pH recording catheter [16–18]. The response time of the ≈ 0.7 μm thick pH responsive copolymer is but a few minutes, allowing rapid characterization of changing pH levels.

It should be noted that the passive, wireless nature of the sensor platform would make it of great utility for long-term monitoring of conditions inside sealed containers, such as food or medicine packages. Magnetoelastic sensor arrays could be combined with any number of chemically responsive layers, and pattern recognition algorithms, to simultaneously measure many parameters remotely from a complex environment.

Acknowledgments

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