

# Application of the quartz crystal microbalance to measurement of the concentration of electrolyte in lead/acid batteries

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## Abstract

The density of the electrolyte in a lead/acid battery may change by 10 to 20% during the discharge/charge cycle and the value within this range can be used as an indication of the fraction of available energy stored in the battery. We describe the application of a quartz crystal microbalance to the determination of the density of sulfuric acid solutions over a range of temperatures and during the discharge of a typical lead/acid battery. The sensor response varies linearly with temperature, and in a quadratic manner with the density of the solution. Good agreement with the theoretically predicted behaviour of thickness shear mode oscillators immersed in liquids was observed. The sensor performed well in the laboratory experiments under artificial conditions. By contrast, initial studies using the sensor in a lead/acid battery operating under real conditions revealed that stray capacitances can influence the stability of the oscillator.

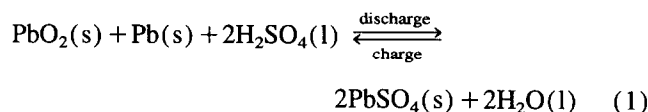
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## 1. Introduction

Most conventional diesel-electric submarines have no automatic system to monitor the state-of-charge of the batteries, even though it is the residual state-of-charge that can limit the underwater endurance of the vessel. The same situation applies to most other types of battery-powered vehicles. Thus, a clear need exists for a method that allows determination of the true state-of-charge to obtain a continuous and reliable estimate of the range of the boat or vehicle.

There are various methods that have been investigated for the measurement of the energy stored in lead/acid batteries and these can be divided into two categories. The first category includes all techniques that check the state-of-charge by determining the concentration of the sulfuric acid in the solutions in the battery cells. The second category uses some electrical characteristics of the battery, such as impedance, as an indication of the charge state. We are concerned primarily in this work with measurements of the first category since they are relatively simpler to implement.

The overall reaction for a lead/acid battery, that gives rise to a change in the sulfuric acid concentration, is as follows:



As an example, the density of the electrolyte in a typical automotive (SLI) battery may vary from about  $1.28 \text{ g cm}^{-3}$  (37% sulfuric acid) in the fully charged state to less than about  $1.15 \text{ g cm}^{-3}$  (21% sulfuric acid) in the discharged state. The value relative to this range can be used as an indication of the fraction of available energy that remains in the battery. Furthermore, the rate of change of the density as charging or discharging taking place can also be a useful indicator of the condition of the battery. The most common means of measuring the density is the conventional, hand-operated, float-type, hydrometer. In practice, this method is not suitable for submarine applications because it does not produce a continuous output and is tedious to apply manually. A variety of devices have therefore been assessed for their ability to produce a signal that varies continuously as the concentration of the sulfuric acid in the battery cells fluctuates during charging and discharging.

Desirable characteristics of candidate sensors are that they should not be subject to interferences, no modification to the battery case should be needed, and they must be absolute sensors. Methods described in the literature range from automated measurements of the density using a hydrometer [1],

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to physical methods where some property of the measuring system is influenced by the density, such as sound propagation [2] and vapour pressure [3]. The most popular methods, however, appear to be those based on potential and light measurements. Tsubota and co-workers [4,5], Cavaliere [6] and Spaziante et al. [7] have all developed a Pb/PbO<sub>2</sub> electrode to measure the concentration of sulfuric acid. Generally, linear relationships exist between the measured potential and the electrolyte concentration, but the response time is found to be long (e.g., 10 to 20 min reported by Tsubota [4]). Furthermore, PbO<sub>2</sub> is consumed during measurements and periodic recharging of the sensing electrode is required.

Hancke [8] has described a probe based on fibre optics. This relies on the principle that intensity losses occur in the optical fibre when it is bent beyond some critical radius. The relative intensity of the light detected at the receiver after passing through a H<sub>2</sub>SO<sub>4</sub> solution was shown to be proportional to the refractive index of the acid which, in turn, was proportional to the concentration of the acid. This method was sensitive to errors introduced by source intensity variations, variable losses in the fibres and connectors, and sensitivity changes in the detector. These error sources could be compensated for by using a reference signal or periodic calibration. An eloquent and simple method of determining the density was described by Derouin et al. [9]. Their method involved directing the beam of a source (i.e., light-emitting diode) into a sheet of glass or other transparent medium immersed in the H<sub>2</sub>SO<sub>4</sub>. When the light impinges on the glass/acid interface, the wavefront of the light is spread out sufficiently to cover a range of incident angles. Any light with an angle greater than the critical angle (dependent on the density) will be internally reflected to a diode-array detector. The position at which the light beam falls on the detector will change as the density of the acid changes. Such a system offers the following advantages: (i) no moving parts; (ii) only the glass medium is in the acid, and (iii) no sensitivity problems due to shock or vibration. Two possible disadvantages are: (i) air bubbles or other battery precipitates attached to the glass might interfere with the measurements, and (ii) a slot must be cut in the battery case to allow insertion of the plate. Unfortunately, despite many attempts to produce a reliable apparatus, none of these methods has so far gained acceptance as an in situ state-of-charge sensor.

Acoustic wave oscillators have long been used as a means of controlling frequency in a wide range of electronic equipment that includes selective filters, computers, communication devices, and timing appliances. It has also been demonstrated that it is possible for acoustic wave devices, such as the quartz crystal resonator, to oscillate whilst in contact with liquids. Furthermore transistor–transistor logic (TTL)-based circuitry has been developed that facilitates relatively simple and reliable measurements of frequency in the liquid phase, and an elementary relationship exists between the frequency shift and the absolute viscosity and density of the solution. We have therefore adapted these devices for the direct and continuous measurement of the

state-of-charge of batteries and, in this paper, we report the use of the quartz crystal microbalance as a means of measuring the density of the electrolyte within a lead/acid battery.

## 2. Experimental

The 10 MHz AT-cut quartz crystals used in this work were obtained from Daintree Industries, Melbourne, and from International Crystal Co., Oklahoma. These crystals had a diameter of 15 mm with centrally deposited keyhole-shaped gold electrodes on both faces. They were used in a configuration (shown in Fig. 1) in which only one side of the crystal is exposed to the acid. This allowed easy immersion of the device into laboratory solutions, as well as the cells of a standard 12 V lead/acid automotive battery. Here, the quartz crystal (1) is attached to a glass tube (7) of the appropriate diameter by means of a sealant (6). An electrical path from the exterior electrode (2) to the inside of the tube was made, and both gold faces of the crystal were attached to the electrical circuit (5) via an electrically conducting polymer.

A block diagram of the basic unit of the oscillator circuit is given in Fig. 2. The circuit is a simple and inexpensive design that consists of half a 7404 hex inverter chip, two resistors, a capacitor, an inductor, and the crystal [10]. The function of the crystal, apart from its purpose as the sensing element, is to act as a band-pass filter for the signals that pass through the feedback path from output to input of the invert-

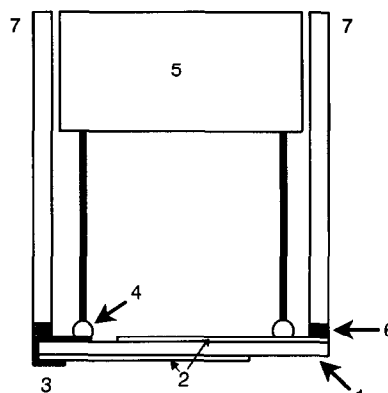


Fig. 1. Drawing of main elements of the sensor: (1) quartz crystal; (2) oscillator electrodes; (3) silver-containing conducting paint; (4) silver epoxy; (5) oscillator electronics; (6) neutral silicone sealant, and (7) glass tube.

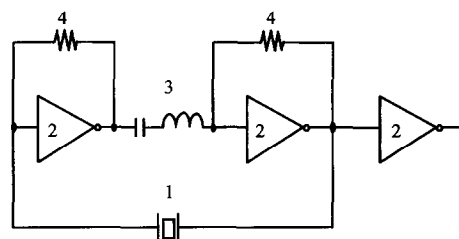


Fig. 2. Block diagram of basic oscillator circuit: (1) quartz crystal; (2) three logic inverters; (3) inductance–capacitance tuning circuit, and (4) two resistors.

ers, i.e., it will block all signals that have frequencies outside a narrow band around 10 MHz. The inverters are used for their amplification properties and convert 5 V signals into a 0 V signal, and vice versa. This amplification is a necessary part of the oscillator circuitry. The resistors used were 560  $\Omega$  low power types. Their precise value in this circuit is not critical. Graf [10] and Barnes [11] indicate that any value between 380 and 680  $\Omega$  will function effectively. These resistors are important because they provide bias voltages and currents that keep the inputs to the two left-hand inverters constantly at around 2.5 V otherwise their negative amplification would push them either to 0 or 5 V and no oscillations could occur at all.

The tuning circuit is of the simplest possible kind. By connecting a capacitor and inductor in series, a rudimentary band-pass filter can be formed. The capacitor blocks low frequency signals and the inductor blocks high frequency signals. Somewhere in between this combination has zero impedance, and this frequency can be calculated via the formula [12]:

$$f = \frac{1}{2\pi} \frac{1}{\sqrt{LC}} \quad (2)$$

where  $L$  is the inductance and  $C$  the capacitance. Evaluating this expression with the values of  $L$  and  $C$  used in the circuit, i.e.,  $L = 10 \mu\text{H}$  and  $C = 22 \text{ pF}$ , the zero impedance point, or resonant frequency, is around 10 MHz. The reason why a band-pass filter is needed is related to the various modes in which a crystal can oscillate. This circuit is designed to force the crystal to oscillate in its fundamental, i.e., lowest frequency mode.

The circuit formed part of an overall configuration that included a reference oscillator circuit in a design similar to that described by Bruckenstein and Shay [13]. Part of the circuit was miniaturized so that it could be inserted into the glass tube that housed the quartz crystal and then placed as close as possible to the crystal. The remainder of Bruckenstein and Shay's circuit, namely the frequency divider and opto-isolator, was located in an all-metal box mounted at the other end of the glass tube. A frequency meter and a frequency-to-digital converter, attached to an IBM-compatible computer, were used to measure and record the frequency difference at the output of the opto-isolator.

Measurements were performed using standard solutions of sulfuric acid contained in glass test tubes, and also in situ using one cell of a 12 V automobile battery. The standard solutions of the appropriate density were prepared by diluting a stock solution of AR grade sulfuric acid with distilled water. In all cases, the densities of the various solutions were measured with an Anton Paar DMA 35 ultrasound digital density meter. During the various measurements, the acid solutions were maintained at the appropriate temperature by means of a water bath controlled to within  $\pm 0.2^\circ\text{C}$ . The in situ battery measurements were performed at room temperature during current discharge through a 0.8  $\Omega$  power resistor. The sensor

was immersed in the electrolyte by one of the filler holes in the top of the battery casing, and both voltage and frequency were monitored during the discharge.

### 3. Results and discussion

The frequency change observed for a quartz crystal immersed in acid solutions of known density at temperatures from 10 to 50  $^\circ\text{C}$  is shown in Fig. 3. While a non-linear relationship exists between the measured signal and the solution density, an almost linear relationship could be obtained if the frequency change was plotted as a function of the density squared, as in Fig. 4.

The frequency change,  $\Delta f$ , observed when a quartz crystal is immersed in a solution with a known absolute viscosity,  $\eta$ , and density,  $\rho$ , is given by the following theoretically derived equation [14]:

$$\Delta f = -2.26 \times 10^{-6} n f^{3/2} (\eta \rho)^{1/2} \quad (3)$$

where  $f$  is the fundamental frequency of the crystal and  $n$  ( $= 1$ ) is an integer equal to the number of faces in contact with the liquid. Eq. (2) predicts that a plot of  $\Delta f$  versus

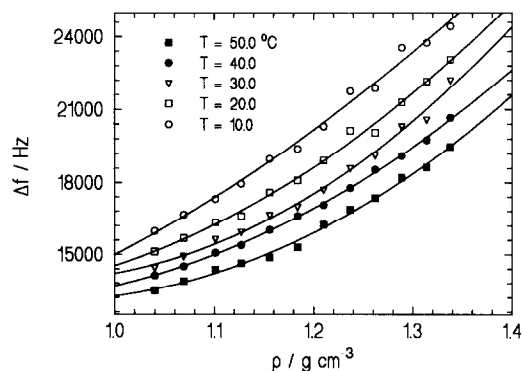


Fig. 3. Oscillator frequency vs. density of sulfuric acid solutions at different temperatures. The lines represent quadratic curves of best fit.

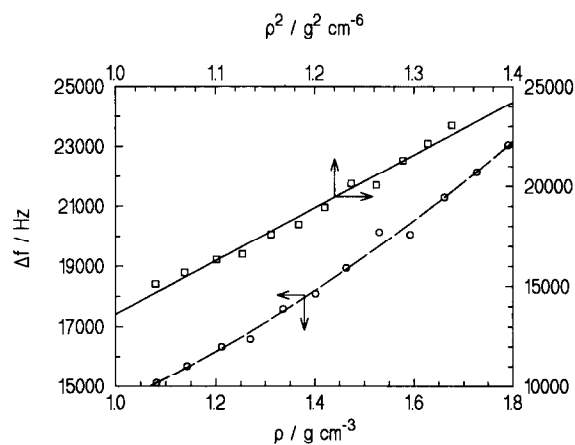


Fig. 4. Oscillator frequency vs. density, and density squared, of a sulfuric acid solution at 20  $^\circ\text{C}$ . The lines represent curves of best fit: (---) is a quadratic curve ( $\Delta f = 1.06 \times 10^4 - 46.7\rho + 3.91 \times 10^3 \rho^2$ ), and (—) is a straight line ( $\Delta f = -1.29 \times 10^4 + 2.65 \times 10^4 \rho^2$ ).

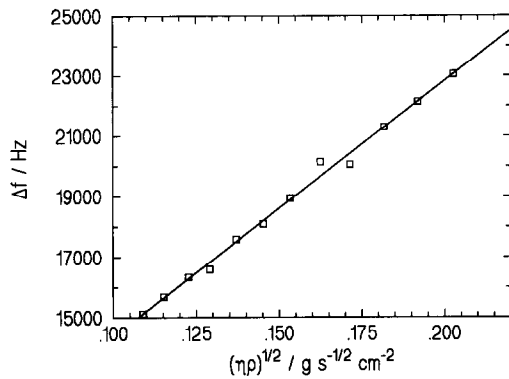


Fig. 5. Oscillator frequency vs. product  $(\eta\rho)^{1/2}$  for experimental data displayed in Fig. 4. The line represents the straight line of best fit:  $\Delta f = 5.9 \times 10^3 + 8.5 \times 10^4 (\eta\rho)^{1/2}$ .

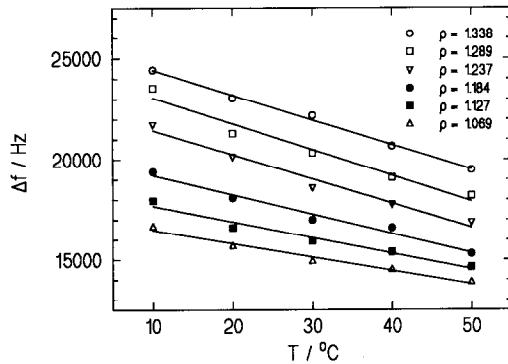


Fig. 6. Oscillator frequency vs. temperature of sulfuric acid solutions of known density ( $\text{g cm}^{-3}$ ). The lines represent straight lines of best fit.

$(\eta\rho)^{1/2}$  should therefore be a straight line. Using some of the experimental data presented in Fig. 3, for which solutions the viscosity values are available in the literature [15], good agreement with Eq. (2) is observed, as shown in Fig. 5. The non-zero intercept arises from the fact that the frequencies (measured in the air) from the reference and sensing crystal circuits, used to calculate  $\Delta f$  electronically, were not identical due to the incorporation of a frequency-pulling capacitor in series with the reference crystal [13].

For the 10 MHz crystals used in this work, Eq. (2) predicts a value for the slope of  $7.15 \times 10^4 \text{ g}^{-1} \text{ cm}^2 \text{ s}^{-1/2}$ , whereas the actual slope is determined to be  $8.47 \times 10^4 \text{ g}^{-1} \text{ cm}^2 \text{ s}^{-1/2}$ . Differences between the theoretical and experimental values have been attributed to the breakdown of the approximations assumed in deriving Eq. (2) and to other factors such as surface roughness [16]. Note that greater sensitivity (i.e., greater frequency change per unit change in  $(\eta\rho)^{1/2}$ ) can be obtained if crystals with a higher fundamental frequency are employed.

To perform density measurements within a lead/acid battery, the sensor must be calibrated over the temperature range of interest. Fig. 6 displays the  $\Delta f$  versus  $\rho$  for different temperatures between 10 and 50 °C. All these curves are non-linear but, as shown in Fig. 6, they can be made almost linear by plotting  $\Delta f$  versus  $\rho^2$ . Plots of  $\Delta f$  versus temperature at various densities, shown in Fig. 3, are straight lines. There-

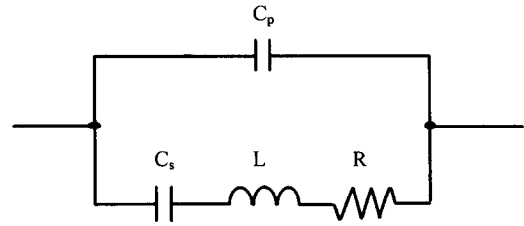


Fig. 7. Electrical equivalent circuit of a thickness shear mode quartz crystal.

fore, the unknown density in a lead/acid battery could be obtained by two linear interpolations into a matrix that consists of values for  $\Delta f$  at different temperatures and  $\rho^2$  values. If greater accuracy were required, a matrix of  $\Delta f$  at different temperatures and densities would be used and quadratic ( $\Delta f$  versus  $\rho$ ) and linear ( $\Delta f$  versus  $T$ ) interpolations would be applied to obtain the unknown density.

A quartz crystal may function either as a series resonant circuit or as a parallel resonant circuit [11]. The equivalent electrical circuit is shown in Fig. 7. At some frequency  $f_s$ , the equivalent capacitance  $C_s$  and the inductance will resonate in the series mode. At a slightly higher frequency  $f_p$ , the crystal functions in a parallel resonant mode whereby the capacitances  $C_s$  and  $C_p$  combine to form a total capacitance. The frequencies are given by the following expressions [17]:

$$f_s = \frac{1}{2\pi} \left( \frac{1}{LC_s} \right)^{1/2} \quad (4)$$

$$f_p = \frac{1}{2\pi} \left( \frac{1}{LC_s} + \frac{1}{LC_p} \right)^{1/2} \quad (5)$$

The parallel, or 'static', capacitance arises because of the dielectric constant of the quartz, and also the capacitance through the surrounding medium and the crystal-connecting leads.

Oscillator circuits have been designed to excite either one or the other mode of oscillation of the crystal. The attributes of a range of electrical circuits for under-liquid sensing applications, including the type used in the present work, have been discussed by Barnes [11]. It appears that, for circuits in which the crystal is in series with the feedback path, the phase shift through the TTL gates is zero and the circuit should excite the series resonant mode. Nevertheless, when the probe was initially used to measure the density of the electrolyte in a lead/acid battery there were instabilities, apparently due to stray capacitances (i.e.,  $C_p$ ) acting on the system. More reliable operation was obtained by shielding both the crystal and the lead/acid battery, and isolating the measuring circuitry by powering it from batteries. Presently, the oscillator circuit is being redesigned so as to ensure that the crystal oscillates only in the series mode and is less susceptible to external electrical effects.

Data obtained from the change in crystal oscillation frequency and battery voltage for a typical discharge are given in Fig. 8. The transformed results show the reduction in electrolyte density during discharge and are consistent with meas-

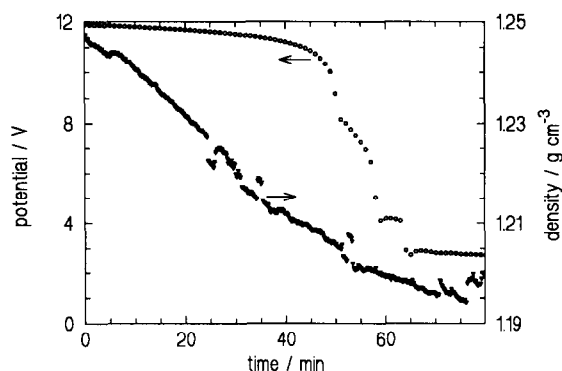


Fig. 8. Change in battery terminal voltage, and electrolyte density measured using a quartz crystal immersed in battery electrolyte during discharge of a typical 12 V automotive battery.

measurements obtained using the series of solutions prepared from the sulfuric acid standard.

#### 4. Conclusions

Compared with other devices proposed as density sensors, the present sensor, and certain optical sensors, do not suffer from the limitations associated with potentiometric sensors (sluggish response and the need for occasional refurbishment or the ultrasonic methods (expensive processing electronics). The quartz crystal sensor has one major advantage over optical sensors in that it can be made to be an absolute method for determining density, because the variation in fundamental frequency from one crystal to the next is minimal. Where high accuracy is required, these slight variations in fundamental frequencies for different crystals, together with changes in frequency due to mounting the crystal in the sensor housing, can be eliminated by performing one calibration measurement. On the other hand, optical sensors require that a number of calibration measurements be performed before the sensors can be used to determine the acid concentration. Provided the effect of stray capacitance can be eliminated entirely, the resultant quartz crystal microbalance sensor should be an ideal tool for determining the density of the electrolyte within a lead/acid battery.

The concepts in this paper have been presented for publication in the patent literature [18] and a recent patent by Japanese workers describes a similar device [19].

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