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Quartz Resonator State-Of-Charge Monitor For Lead-Acid Batteries*

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We have demonstrated that a thickness shear mode (TSM) quartz resonator can be used as a real-time, *in situ* monitor of the state-of-charge of lead-acid batteries. The resonator is sensitive to changes in the density and viscosity of the sulfuric acid electrolyte. Both of these liquid parameters vary monotonically with the battery state-of-charge. This new monitor is more precise than sampling hydrometers, and since it is compatible with the corrosive electrolyte environment, it can be used for *in situ* monitoring.

A TSM resonator consists of gold electrodes deposited on opposite surfaces of a thin AT-cut quartz crystal (Fig. 1a). When an RF voltage is applied to the electrodes, a shear strain is introduced in the piezoelectric quartz and mechanical resonance occurs between the surfaces (Fig. 1b). A liquid in contact with one of the quartz surfaces is viscously entrained, which perturbs the resonant frequency and resonance magnitude. If the surface is smooth, the changes in both frequency and magnitude are proportional to $(\rho\eta)^{1/2}$, where ρ is the liquid density and η is the viscosity [1,2].

The active materials in a lead-acid battery are lead oxide (PbO_2) on the positive plates, porous lead (Pb) on the negative plates and dilute sulfuric acid (H_2SO_4) as the electrolyte. During the discharging and charging of the battery, the chemical reaction in each cell is described by

$$\mathbf{PbO_2\ (Anode)\ +\ 2\,H_2SO_4\ (Electrolyte)\ +\ Pb\ (Cathode)}$$
$$\mathbf{discharge} \downarrow \uparrow \mathbf{charge}$$
$$\mathbf{PbSO_4\ (Anode)\ +\ 2\,H_2O\ (Electrolyte)\ +\ PbSO_4\ (Cathode)}.$$

The concentration of sulfuric acid in the electrolyte changes significantly with the battery state-of-charge. Approximate concentration ranges for fully charged and discharged states are shown along the abscissa in Fig. 2.

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* This work was performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000.

+ On Contract from Ktech Corporation, Albuquerque, NM.

Both the density and viscosity of the battery electrolyte vary with the H_2SO_4 concentration. Literature values of these two parameters are plotted (solid lines) in Fig. 2. Traditionally, electrolyte density has been used to indicate state-of-charge in a lead-acid battery, although viscosity exhibits a much stronger dependence on acid concentration (5.5 times the sensitivity at 40% H_2SO_4). The quartz resonator response, proportional to $(\rho\eta)^{1/2}$, is also plotted. Figure 2 shows that density-viscosity values measured with the quartz monitor (circles) agree with literature values (solid line). Because of the conductivity of the sulfuric acid, only one surface of the quartz resonator can be exposed to the liquid to avoid "shorting" between electrodes.

In a laboratory demonstration, a small 12V lead-acid battery was discharged and recharged several times in succession. The electrolyte in one cell was continuously pumped across the surface of the quartz resonator. A specially-designed lever oscillator circuit drives the resonator and provides the electrical signals for monitoring the frequency shift and the damping magnitude [3]. (Damping is introduced by the motional resistance of the viscous liquid.) Periodically, the electrolyte specific gravity was measured using a float hydrometer. Since density and viscosity are temperature dependent, a separate measurement of temperature was also made.

Four parameters extracted from one discharge cycle in the test series are plotted in Fig. 3. The quartz oscillator voltage tracks quite precisely both the electrolyte specific gravity and the estimated charge content (battery discharge current × time). Estimating the charge alone could be used to indicate state-of-charge, except this parameter can be highly charge/discharge-rate dependent and initial charge conditions must be known *a priori.* The battery voltage is also plotted in Fig. 3. This parameter is not a good measure of the state-of-charge, showing little deviation for most of the discharge cycle and then falling catastrophically as the charge depletes. The correlation among the estimated charge capacity of the battery, the electrolyte density and the measured quartz monitor voltage is quite high. Coefficients for pairings of these parameters are given in Table 1. These high correlation coefficients are an indication this monitor has the potential for accurately measuring state-of-charge.

The shift in resonant frequency of the monitor proved to be an unreliable measurement for determining electrolyte density-viscosity and, consequently, battery state-of-charge. Small quantities of lead oxides and salts from the electrolyte intermittently settled onto the resonator surface. This produced a frequency shift due to the accumulated surface mass [2]. Oscillator voltage, which depends only on the viscous damping contributed by the liquid, does not respond to these changes in surface mass. Thus, a simple oscillator damping measurement is all that is required for this monitor.

The TSM quartz resonators are small in size and can be easily configured for *in situ* monitoring in the lead-acid cells. Real-time metering of state-of-charge in electric vehicle batteries and critical industrial backup power stations is proposed.

[1] H. Muramatsu, E. Tamiya and I. Karube, *Anal Chem*, **60**, 2142-2146 (1988).
[2] S. J. Martin, V. E. Granstaff and G. C. Frye, *Anal Chem*, **63**, 2272-2281 (1991).
[3] K. O. Wessendorf, *Proc. 1993 IEEE Intl. Freq. Control Symp.*, 711-717 (1993).

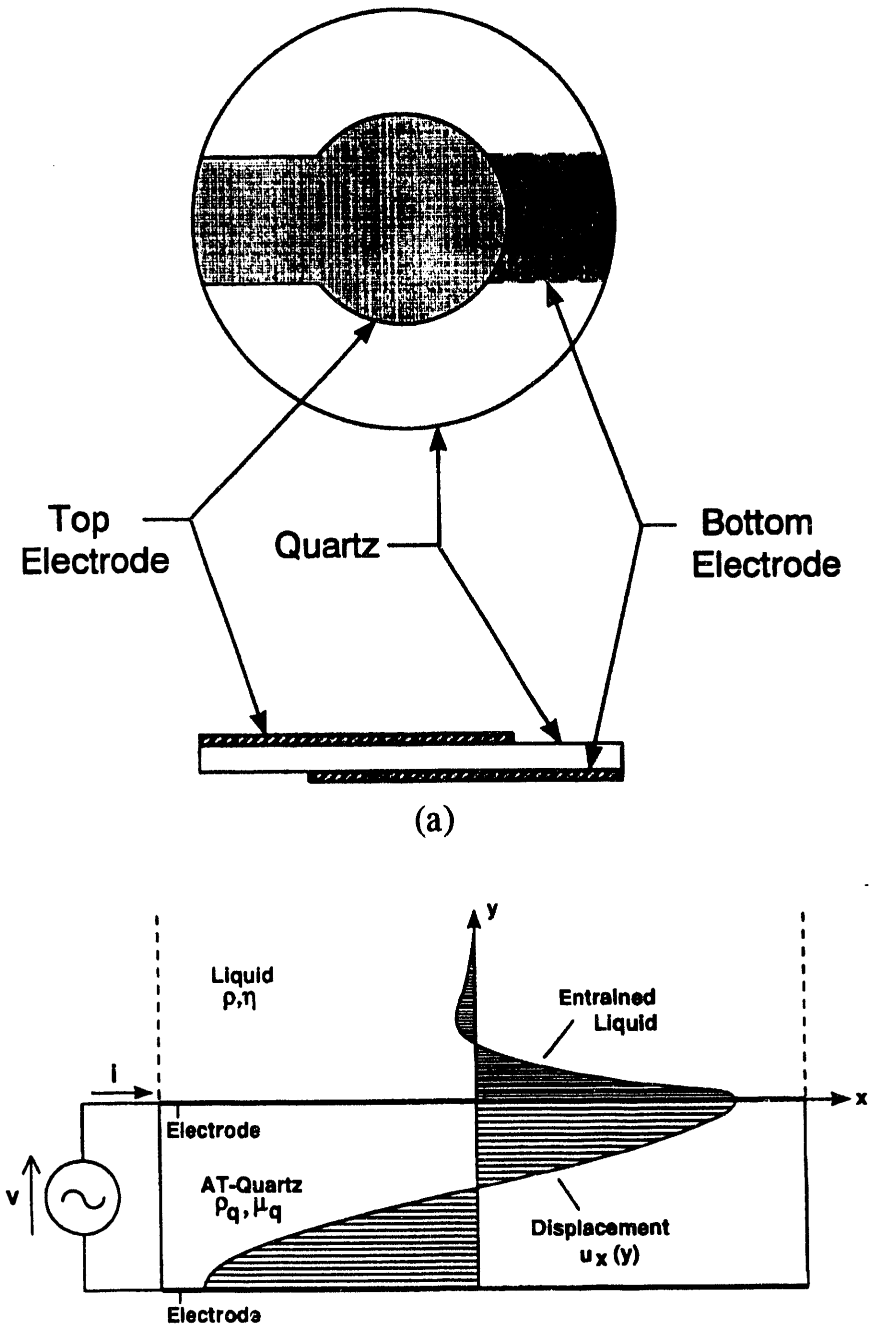

Figure 1. *(a) Top and side views of a TSM quartz resonator. (b) Shear motion in the bulk quartz and the viscously-entrained liquid.*

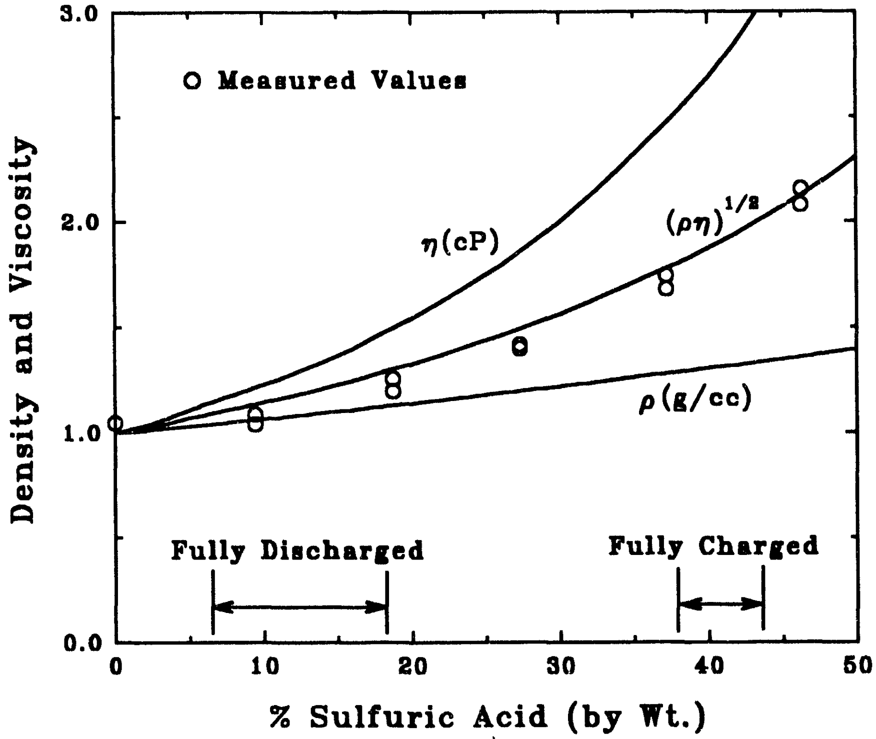

Figure 2. Parameter variations for the electrolyte in a lead-acid cell as a function of the sulfuric acid concentration.

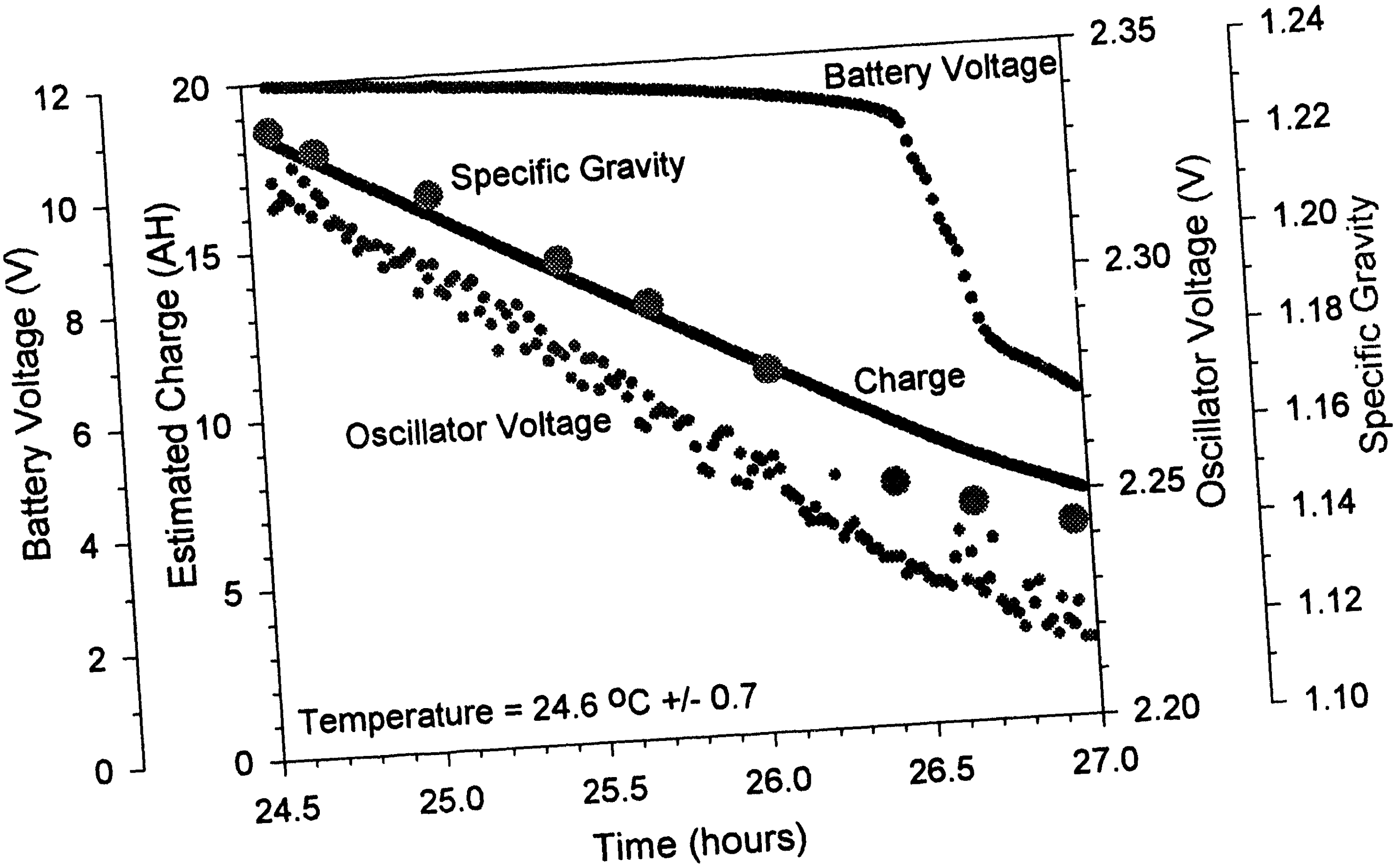

Figure 3. Changes in the battery parameters and the sensor voltage output versus time for one deep discharge cycle in a test series.

Table 1. Correlation coefficients among three of the battery and sensor parameters plotted in Fig. 3

Correlating Parameters	Coefficient
Specific Gravity ↔ Estimated Charge	0.982
Oscillator Voltage ↔ Estimated Charge	0.984
Specific Gravity ↔ Oscillator Voltage	0.993

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