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Refractometric Sensing of H_2SO_4 Specific Gravity in Lead-Acid Cell Operation

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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION AND BACKGROUND	1
THEORY	1
Refractive Index	1
The Lead-Acid Cell	3
An Automatic Refractometric Sensor	4
EXPERIMENTAL METHODS	4
RESULTS AND DISCUSSION	5
ACKNOWLEDGMENT	8
REFERENCES	8

ABSTRACT

A simple inexpensive dipping refractometer for continuous automatic monitoring of the refractive index of fluids has been used to record the changes in electrolyte specific gravity during cycling of a lead-acid cell. It introduces no contamination, is durable, and minimizes test sampling and personal attendance. It may be adapted for automatic control systems and can be operated as a level indicator.

PROBLEM STATUS

This report concludes one aspect of the problem; work on other phases is continuing.

AUTHORIZATION

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REFRACTOMETRIC SENSING OF H_2SO_4 SPECIFIC GRAVITY IN LEAD-ACID CELL OPERATION

INTRODUCTION AND BACKGROUND

Testing and monitoring submarine storage batteries requires the expenditure of considerable effort and funds. Because a large number of cells are under observation at any given time, it is most convenient to employ automatic equipment to record data on individual cells. This has been accomplished to a large extent; however, the registration of electrolyte specific gravity has not been automated. Since electrolyte specific gravity is indicative of the state of charge of a battery or of battery condition (i.e., whether charged, internally shorted, self-discharging at abnormally high rates, accepting charge, etc.), it is mandatory that the electrolyte be monitored (1,2). In the absence of automation and because the number of cells is large, pilot cells are used for measuring specific gravity, and the values are taken as averages for an entire battery. It is necessary to secure the charge when taking these measurements under circumstances which might involve fire hazards.

Any method for routinely measuring electrolyte specific gravity requires that no contamination be introduced into the cell, that the amount of electrolyte consumed in the test be negligible, and that the cost and difficulty of making the test measurements be within reasonable limitations. In order to warrant a change in present procedure any new technique must offer significant improvement over present methods of operation.

While observing an operational demonstration of a simple refractometric sensing device (3) the author recognized that the instrument might be useful for electrolyte monitoring during cycling of the lead-acid cell. Arrangements were made with the inventor of the instrument to borrow it for a brief feasibility study. The purpose of this report is to show that the instrument is suitable for automatic electrolyte monitoring in the lead-cell and should be considered for application in battery installations where automatic recording of cell data is desired.

THEORY

Refractive Index

Refractive index is a fundamental characteristic of materials and is widely used to identify pure compounds and to characterize certain solutions (4-13). Tabulations of the relation of composition of aqueous solutions of many materials to their density, refractive index, and other concentrative properties appear in chemical handbooks; some examples are shown in Fig. 1 (14,15). The relationship of density* to refractive index is expressed by the Lorenz-Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = dr_L , \qquad (1)$$

*For all intents and purposes in storage battery applications density may be considered synonymous with specific gravity (1).

where

n = index of refraction,

d = density, and

r_L = a constant, known as the specific refraction,

which is valid over extended concentration ranges for most solutions. Because refractive effects are related to the interaction of fundamental particles of matter (atoms, ions, and molecules) with electromagnetic radiation, deviations from linearity as expressed in the equation are indicative of compound formation or other structural chemical change.

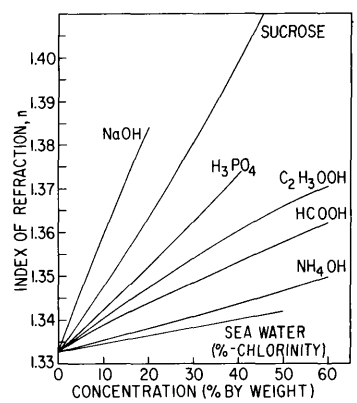

Fig. 1 - Index of refraction relative to the concentrations of aqueous solutions of seven compounds. Concentrations are given in weight-percent except for sea water which is given in percent chlorinity. The data are taken from Ref. 15.

The characteristic index of refraction for a material is the ratio of the speed of light in the given medium relative to the speed in air or vacuum as a standard. The relative refractive index for light traveling from one medium to another across the interface between the two may be found from the ratio of their characteristic refractive indices. When light traveling in highly refractive material impinges on an interface with a less refractive material, it may or may not pass across the boundary, depending upon the angle at which the rays strike the interface. If a ray does not traverse the interface it is said to be internally reflected. The angle at which a ray traveling in the optically dense medium is refracted along the interface between the two media is called the critical angle Φ, indicated by the lines marked C and N in Fig. 2. The magnitude of Φ is a function of the relative refractive index between the two media:

$$\sin \Phi = n_L/n_g, \tag{2}$$

where

n_L = index of refraction of the less refractive medium,

n_g = index of refraction of the more refractive medium, and

Φ = critical angle for a ray traveling in the more refractive medium, measured from the normal to the interface.

This relationship, known as Snell's Law, forms the basis for the design of many refractometers. From Eq. (2), when the more refractive medium is a chosen material of reference, such as glass with $n_g > 1.5$, the critical angle varies directly with the index of

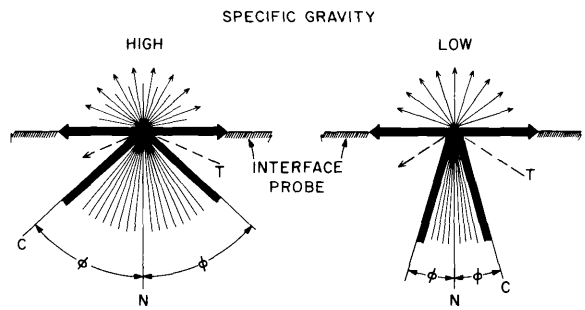

Fig. 2 - Schematic representation of the refractive phenomena occurring at the interface of the glass probe and the solution of sulfuric acid. $\angle\Phi$ is the critical angle measured from the normal N, C is the critical ray that is refracted to travel along the interface and T is the totally internally reflected ray. Any ray making an angle greater than $\angle\Phi$ will be totally reflected. The magnitude of $\angle\Phi$ depends upon the relative index of refraction between the probe and the surrounding medium; the greater $\angle\Phi$, the greater the amount of light that escapes across the interface.

refraction of the second material n_L. Further, from Eq. (1), $\angle\Phi$ is a function of the density (or specific gravity) of the less refractive material.

The Lead-Acid Cell

The reaction of the lead storage cell is

$$PbO_2 + 2H_2SO_4 + Pb = 2PbSO_4 + 2H_2O,$$

charge ← → discharge

and the cells may be used repeatedly because the reaction can be driven in either direction. It is obvious that the concentration of the sulfuric acid electrolyte is at a maximum when the cell is fully charged and at a minimum when discharged. For this reason the specific gravity of the electrolyte is used as an indicator of the state of charge, as well as of the "condition" of a cell. For example, an internal short or accumulation of antimony on the surface of the negative plates will permit current to pass through the cell as though accepting charge. If the specific gravity does not rise in its normal fashion it is a signal that the electrochemical conversion of the battery active materials is not taking place. Similarly on discharge, if the specific gravity of the electrolyte does not fall simultaneously with the voltage of the cell, some factor such as grid corrosion or softening of the active materials is preventing the normal discharge reaction. These effects are usually associated with the end of the useful life of a cell and indicate that it must be replaced.

Because of the significance that may be attached to specific gravity readings, it is useful to have a record of them for battery management, but for large installations this

becomes exorbitantly expensive since these readings are usually made by hand. For this reason it is common to read the specific gravity of selected pilot cells, and then only for special tests. The specific gravity is normally measured with a hydrometer by temporarily removing a small sample of electrolyte from the individual cells. When the cells are gassing heavily at the end of charge, special precautions are required to prevent accidents, because the gas mixture is explosive. If the specific gravity determinations could be made automatically, battery operation would be expedited, especially when large numbers of cells must be monitored such as in testing installations, aboard submarines, and in telephone exchanges.

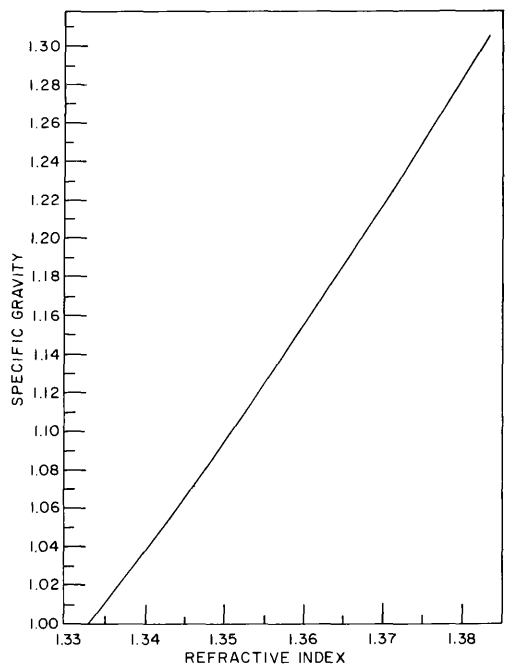

Fig. 3 - Index of refraction as a function of specific gravity of aqueous H_2SO_4 solutions at 20°C. The data are taken from Ref. 15.

Recording instruments have been developed (16-24) that will register changes in electrolyte concentration by following the refractive index of the H_2SO_4 solution, Fig. 3 (6,15,25-27), but they are more complex and precise than required for the application described here. In general these instruments are intended for research or continuous operation with a single material for large volume process control and would not be convenient nor economically feasible for battery applications.

An Automatic Refractometric Sensor

The compact inexpensive dipping refractometer (3) (Fig. 4), consists essentially of a U-shaped rod, the two ends of which are sealed in the mounting head. The head may be of a suitable material and geometry to fit as a plug in any desired container, and the length of the probe is chosen so that the rod is partially or totally immersed in the liquid being monitored. Within the mounting head a miniature light source and photodetector are located at either end of the rod. The amount of light falling on the detector depends upon the loss through the walls of the rod, which in turn is a function of the indices of refraction of the material of the rod and the medium surrounding it. The material of the rod is chosen so that its index of refraction is greater than that of the medium it is used to monitor. Any change in refractive index of the surrounding medium results in a change in the critical angle Φ for the light traveling through the rod (Fig. 2). The higher the refractive index n_L, the larger are both Φ and the amount of light that escapes the rod. Changes in specific gravity of the solution vary the amount of radiation falling on the photodetector. The sharp radius of curvature at the tip of the probe produces an area particularly sensitive to changes in refractive index of the medium. The signal output from the photodetector is converted by conventional instrumentation for registration on standard recorders.

EXPERIMENTAL METHODS

To illustrate the application of this refractometric instrument to lead-acid battery monitoring the probe was fabricated from glass rod, and the light source and photodetector circuit were powered from an external battery, the photodetector replacing one arm

Fig. 4 - Refractometric instrument used in this study (courtesy of Mr. E. Goldstein)

in a bridge circuit. The bridge imbalance was sensed by a Keithley electrometer amplifier-microammeter. The output of this device fed a standard Leeds and Northrup 20 mv multipoint recorder. Initial bridge balance for a null was accomplished by variable resistive arms in the bridge circuit. A number of cells could be monitored at one time by using a probe and bridge circuit for each cell and a nonshorting switch to scan the cells, connected to a recorder through a coupling circuit if necessary.

A commercial 30-amp-hr-cell was used in this work. The cell was charged and the specific gravity adjusted to 1.257. A small hole was drilled in the cell top and the probe was partially submerged in the electrolyte at the edge of the element. The cell was cycled at the 4 and 8 hr rates. During the cycling, samples of electrolyte were temporarily removed at intervals and the specific gravity measured by convention methods. The probe was calibrated by preliminary submersion in a series of standard sulfuric acid solutions. The tests described here were carried out at room temperature. A small sheet of polyethylene was placed in the cell between the probe and the cell element to serve as a deflector for gas bubbles for some of the tests.

RESULTS AND DISCUSSION

Photographs of sections of recorder chart showing the registration of the change in refractive index and cell voltage for a capacity cycle of the cell are shown in Fig. 5. A comparison of this recording with the usual plot of specific gravity readings, cell voltage, and current taken during such a cycle (1) shows that the two are indistinguishable except at the end of charge. When the negative plates began to gas vigorously, the refractometer readings became erratic owing to the hydrogen bubbles in the electrolyte. This effect was completely eliminated by placing a plastic sheet between the element and the probe to shield it from direct impingement of the bubbles.

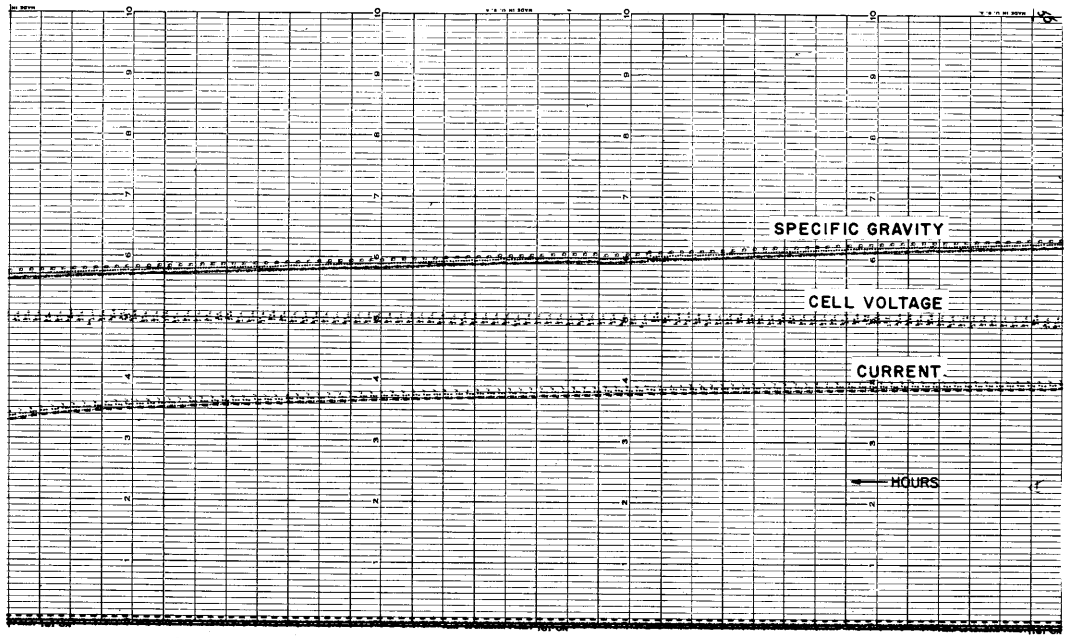

Fig. 5a - Recorder chart showing the automatic plotting of the cell voltage, current, and specific gravity (index of refraction) during capacity discharge of the cell

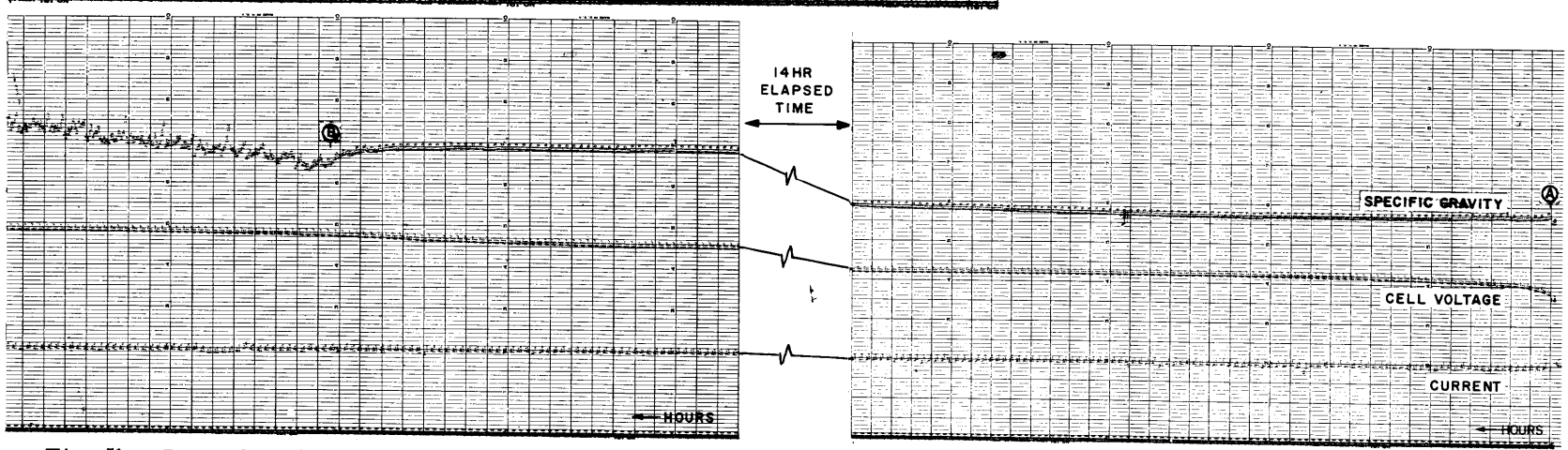

Fig. 5b - Recorder chart showing the automatic plotting of the cell voltage, current, and specific gravity during charge. The transitory deflection of the refractometric recording at A may merit further investigation. B shows the fluctuations produced by impingement of hydrogen gas bubbles on the surface of the glass probe. This occurred as the negative plates began to gas vigorously at the end of charge, and shows the need for protecting the probe from direct impingement of the bubbles. The effect was totally removed by inserting a sheet of polyethylene between the probe and the edge of the cell element. Any design for practical application of this instrument for battery use must provide for elimination of this effect.

Several interesting phenomena were observed during this work which suggest that this instrument or modifications of it may be useful for more fundamental electrochemical investigations. The lead-acid cell used for this test contained no provision for stirring the electrolyte; during charge the positive plates began to gas significantly and, before the negatives finished, the refractive index passed through a maximum. As the charge continued the specific gravity decreased again as mixing took place and ultimately rose to the final and constant value. These effects proceed as follows: a maximum occurs as oxygen bubbles carry high density electrolyte to the top of the cell from the reaction of charge at the positive plate, then a subsequent rise occurs as the negative plates finish charge and began to gas freely, and finally there is a leveling off as the electrolyte becomes thoroughly mixed. The rates of these refractive index changes might be used, under suitable experimental conditions, to measure the difference in rates of charge of the positive and negative plates and in electrolyte diffusion-rate studies.

Immediately upon application of the charge or discharge current the indicator showed a transitory response that may merit further investigation. It is possible that the deflection was caused by differences in the rates of response of the anions and cations to the application of the electric field.

The response time of the device is essentially limited only by the time constant of the photodetector and its associated circuitry. Capillary probes and other special probe geometries may be used, and the sensitive tip may be placed in close proximity to an electrode surface. This suggests a possible use for this instrument in estimating concentration gradients near the surface of an electrode, supplementing Schlieren, interferometric, and analytical techniques (28-30).

Because refractive index is directly related to specific gravity, any factor such as temperature that affects the specific gravity has a corresponding effect on the index of refraction. For temperature correction of specific gravity readings in storage battery operation a rule of thumb is used which is sufficiently accurate for the purpose although it is only an approximate value of the true temperature coefficient. The measured specific gravity is corrected "one point" for each 3°F differential from a standard temperature, usually 80°F. "One point" is a unit in the third decimal place of the specific gravity reading, the usual accuracy in battery electrolyte management (1). Increasing temperature causes expansion of the electrolyte, and a lower specific gravity reading so that the correction must be added to the observed value. The reverse is true at temperatures below the standard, and the actual measurement will be too high. For precise measurement of refractive index it is, of course, necessary to correct the optics for temperature variations, but for lead-acid battery applications, variation of the index of refraction of the glass probe with ambient temperature would not be of sufficient magnitude to necessitate this, and the usual "rule of thumb" may be used for temperature correction of specific gravity read by refractometer or hydrometer.

It is feasible to incorporate within the electrochemical cell a reference probe encased in a tube of standard H_2SO_4, which can function as an internal temperature compensator and standard specific gravity reference. The accompanying circuitry would be designed so that the difference between reference and explorer probes was measured. In this technique, no external temperature correction would be required.

ACKNOWLEDGMENT

Appreciation is extended to Mr. Emmanuel Goldstein,* formerly of the Optical Physics Division of this Laboratory, for helpful cooperation in adapting the recording refractometer to this specific use for batteries, for permission to reproduce the photograph of Fig. 4, and for loan of the instrument used in this work.

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13. ABSTRACT

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