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Applications of Refractometry in Battery State-of-Charge (SOC) Measurements

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Introduction

Conventional measurement of state of charge in open port lead acid batteries is accomplished via hydrometers that measure the specific gravity (SG) of the electrolyte. The specific gravity is proportional to H2SO4 concentration which is the historical gold standard of SOC. One specific drawback of this method is that it requires fluid extraction from the battery. This procedure can be messy, labor intensive and sometimes dangerous. The SOC is determined by comparing the specific gravity measurements to reference levels for that particular type of battery and, on a practical level, can only be employed periodically. Other newer methods rely on battery voltage, charge "bookkeeping" or impedance measurements with greater or lesser degrees of success. The method described herein relies on the direct measurement of the index of refraction of the electrolyte via an optical technique[1]. This device can be directly and semi-permanently inserted into each battery cell thereby providing a continuous readout of SOC. Minor variations in this technique can be used to measure electrolyte levels and cell temperature resulting in a multi-purpose device. We describe the theory of operation and show experimental data that demonstrates stable, accurate and continuous real-time determination of SOC. This paper describes how the relationship of the refractive index of H_2SO_4 solutions to their density or relative concentration can be used to determine state-of-charge. The technique required the development of a unique method of *in situ* measurement of refractive index and adapting it to practical battery measurements [1]

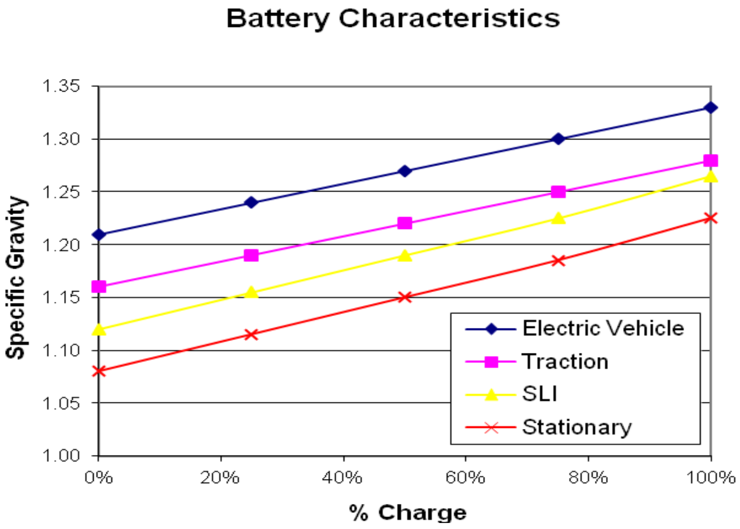


Figure 1. SG relationship to state of charge for several different types of batteries

Figure 1 shows the typical relationship between SG and % state of charge for various battery types. More generally these relationships are specified by the battery manufacturer so that simply knowing SG does not necessarily translate to % SOC which is the relative quantity of energy contained in the battery. Fig. 2 shows the relationship of SG to refractive index as a function of H_2SO_4 concentration. Over this typical range of SGs, the refractive index @ 20ºC, 589nm varies from about 1.36 to 1.38.

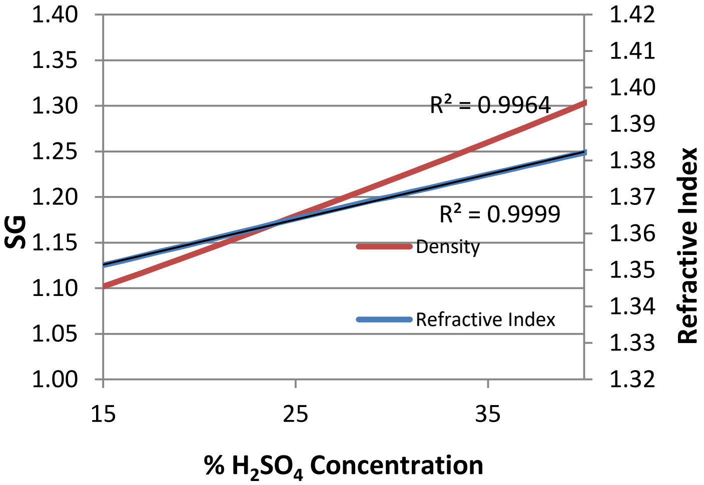


Figure 2. The relationship between SG, electrolyte concentration and refractive index for a typical lead acid battery

The *in situ* measurement of the refractive index of the electrolyte of a typical lead acid battery requires a rather special refractometer and to this end we resort to the theory of optical waveguides.

Optical Waveguides

The simplest optical waveguide is a fiber optic cable whose cross-section is shown in Fig 3. This two component cylindrical device consists of a core which can be glass or a special plastic and a cladding which is basically a coating on the cylindrical core. Light signals generated by a laser or LED are transmitted down the fiber to a receiver.

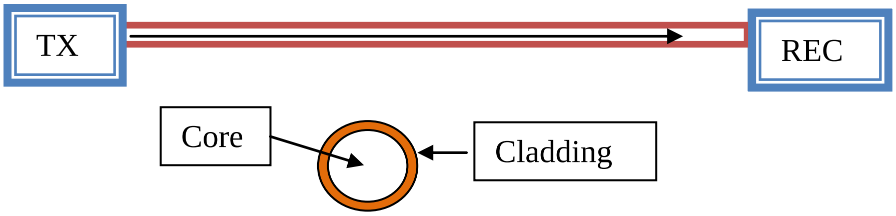


Figure 3. Configuration of an optical fiber

This technology is well developed and is in widespread use to carry telephone calls over long distances. The condition for relatively lossless wave propagation inside such a device is given as:

$$n_c^2 - n_{cl}^2 \geq 0 \quad (1)$$

where $\boldsymbol{n_c}$ is the refractive index of the core and $\boldsymbol{n_{cl}}$ the index of the cladding. As the two indices approach each other in value the guide is progressively less capable of propagating the signal without loss. Fig. 4 shows the relative response of the fiber as the cladding index approaches the core index for two core indices. It is clear that the relative losses of the guide are a somewhat non-linear function of the cladding index. If we figuratively remove the cladding and replace it with a transparent liquid then the response of this imaginary fiber will vary with the index of the surrounding liquid.

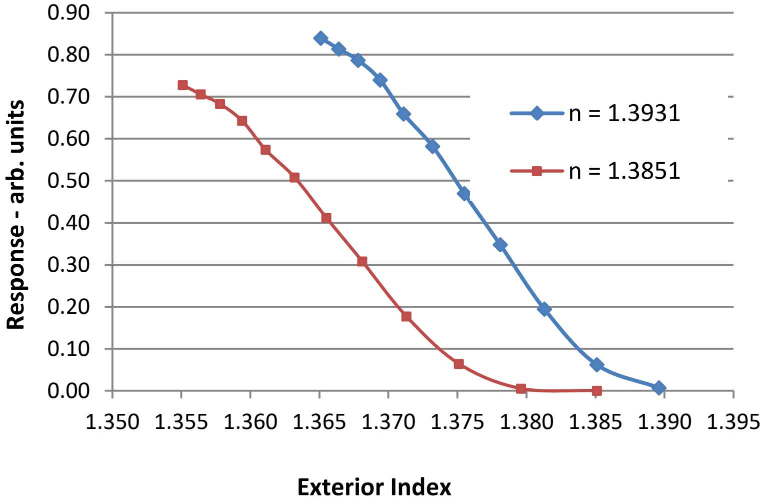


Figure 4. Sensor response vs. cladding index for two different core indices

So as the previous comment implies, choosing an appropriate core index appropriate to the range of indices of interest and substituting a surrounding liquid for the cladding enables a response that is a function of the cladding index. Thus, measuring the relative response of the device enables a measurement of the surrounding liquid index and hence the concentration of H_2SO_4.

In summary, the principle of operation of this sensor concept is analogous to a conventional optical fiber with two novel exceptions: The cladding of the fiber is the liquid under measurement and the core of the fiber may be a liquid in a tube or a solid un-cladded fiber with the appropriate characteristics.

Practical Implementation

In practice, battery acid is a formidable solvent and so anything immersed in the electrolyte has to be acid resistant. Conventional fiber materials are not usable in this application and so we must look to other substances to serve either as a container or the core itself. Most solids react with acid however glass in its many variants is a notable exception. There are no glasses with an appropriate index (around 1.38) for this application however it can be considered for use as a container or coating. As long as the index of the container is greater than the core or cladding it is essentially transparent and does not significantly interact with the properties of the sensor. Consider the configuration shown in Fig. 6 where we have immersed a liquid filled tube with appropriate index in an enclosure filled with battery acid. As the index of the electrolyte changes due to charge or discharge of the battery the transmission of the tube varies as in Fig. 5. It is also clear that if the liquid level of the enclosure changes so does the total response since the condition in Eq. (1) is violated over part of the tube. It is this condition that renders the tube as a level sensor so long as the index of electrolyte doesn't change. Unfortunately, in a battery it is impossible to completely separate these two effects.

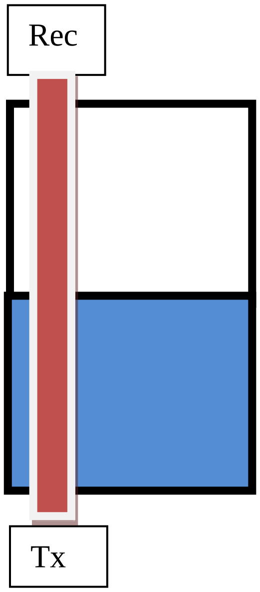


Figure 5. Refractometer configuration in battery cell

The configuration shown in Fig 5 is not practical in a typical open port batteryand so we must resort to another configuration that is independent of electrolyte level. Suppose we look at the configuration shown in Fig 6. The straight through configuration is replaced with a tube containing an end mirror so the light that transmitted into the tube is reflected at the end, recollected by a fiber optical arrangement and piped to a detector. In this case as long as the active length of the sensor remains immersed in the liquid the dependence on liquid is removed.

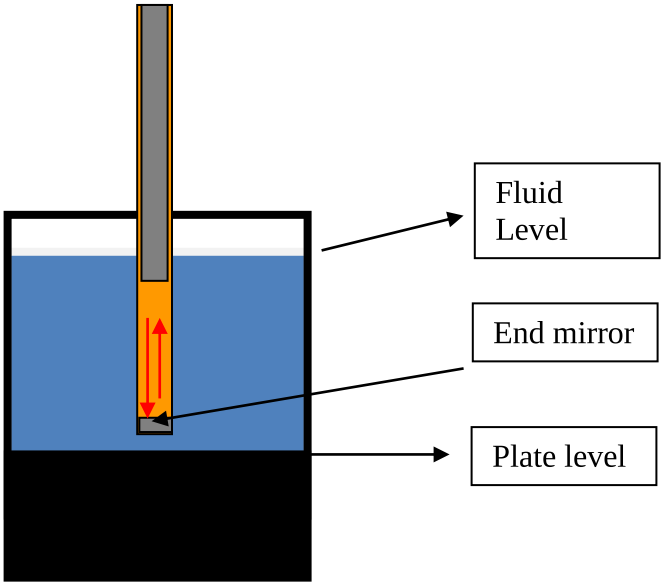


Figure 5. Practical refractometer configuration in battery cell

This is totally the equivalent of maintaining the electrolyte above a certain level in a battery to assure proper operation so this condition is compatible with normal battery operation. An unintended bonus is that when the fluid drops below acceptable levels the sensor output falls off dramatically indicating a fault condition. Two additional topics of interest are temperature dependence and level sensing.

Temperature Dependence

The conventional and widely accepted method of determining the SOC in wet lead acid batteries was by use of a hydrometer that measures the specific gravity of the electrolyte. Since density is both temperature and SOC dependent this factor had to be incorporated in correcting the density reading for these effects. The temperature dependence of the refractometer is much less on the order of a few times 10^{-4} ◦C^{-1}

Calibration

Calibration of the sensor is accomplished via a secondary transfer process. Essentially the sensor output in volts corresponds to an index of refraction of the calibration liquid. A number of data points are taken over an index range corresponding to an electrolyte SG range of 1.1 to 1.35 (n = 1.34 to 1.39.). These indices are reference to the appropriate electrolyte SG via H2SO4 references tables

Actual calibration data for a typical sensor in the configuration of Fig 5 is shown in Fig 6.

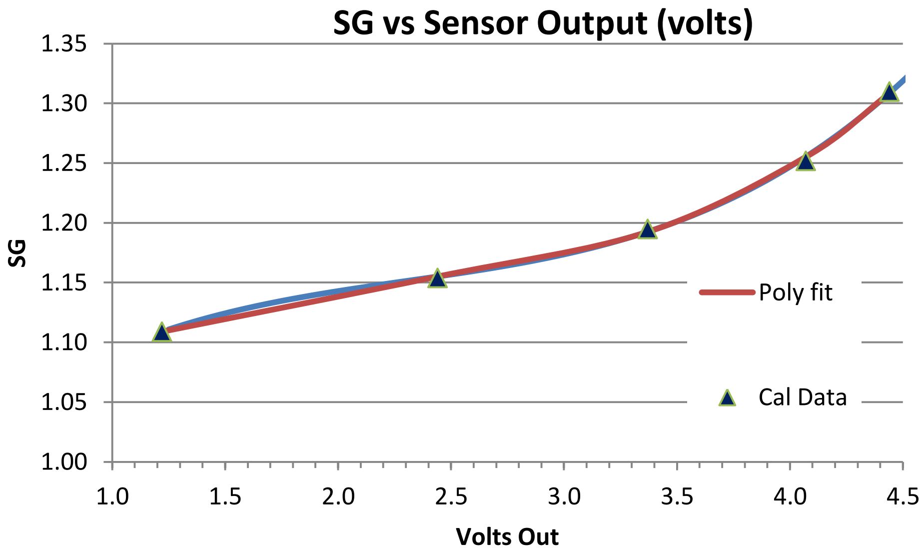


Figure 6. Typical calibration curve for a sensor configuration

It is notable that the dynamic range of this sensor configuration is of the order 100 volts/n

Level Sensing

It has been suggested by the foregoing discussion that this same technique can be used to sense the level of an electrolyte given a constant index i.e. one that is independent of SOC. For reasons stated this is not possible so a slightly different configuration has to be adopted to do level sensing. This is accomplished by changing the internal medium in the tube in Fig 5 such that is insensitive to index variations. Output voltage of such a configuration is shown in Fig 7.. The physics of how and why this works is beyond the scope of this paper.

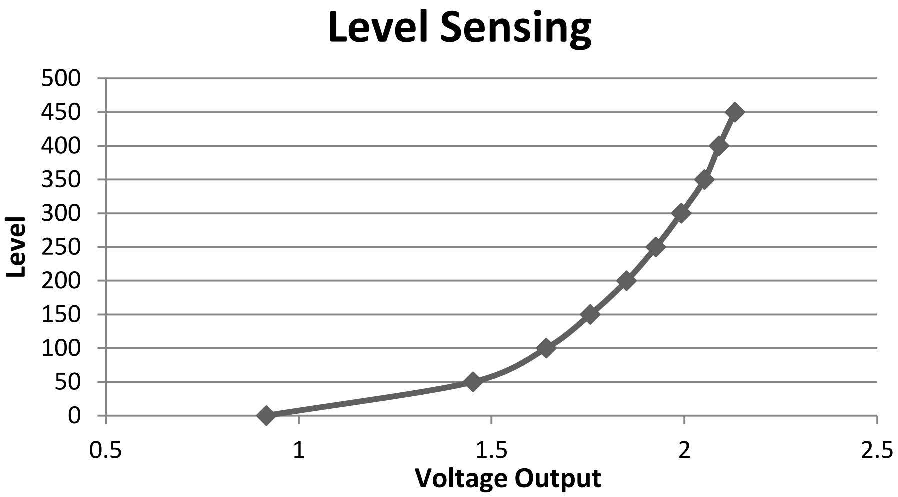
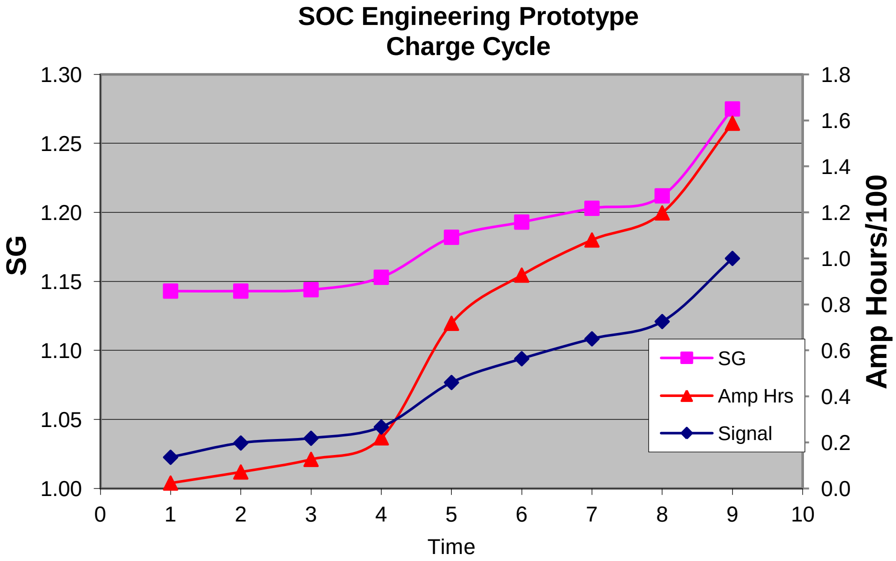
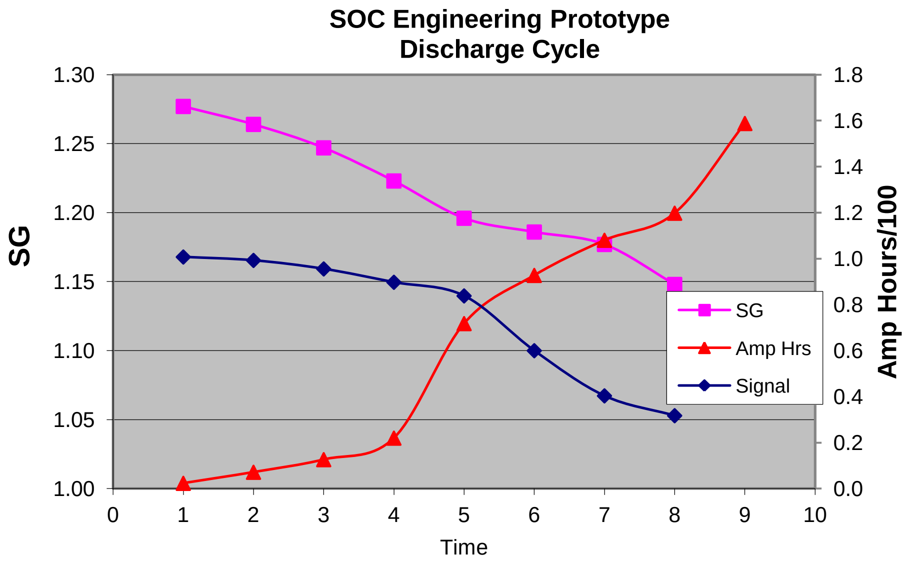


Figure 7. Level sensor output

Actual Battery Test Results





In summary the optical means of state of charge sensing described herein appears to provide a new paradigm in charge sensing for a considerable proportion of the several hundred million lead-acid batteries currently in existence. Eliminating the need for fluid extraction from the cell, the approach provides a rapid, real time capability for SOC determination.

1. US patent 10,145,789, Immersion Refractomter