

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

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## Abstract

Conventional measurement of state-of-charge (SOC) in open port, lead-acid batteries is made via hydrometers that determine the specific gravity of the electrolyte. The specific gravity is the historical gold standard of SOC and is proportional to the concentration of H<sub>2</sub>SO<sub>4</sub>. 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. Newer methods of SOC measurement 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<sup>1</sup>. 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 technology. We describe the theory of operation and show experimental data that demonstrates stable, accurate and continuous real-time determinations of SOC.

## Introduction

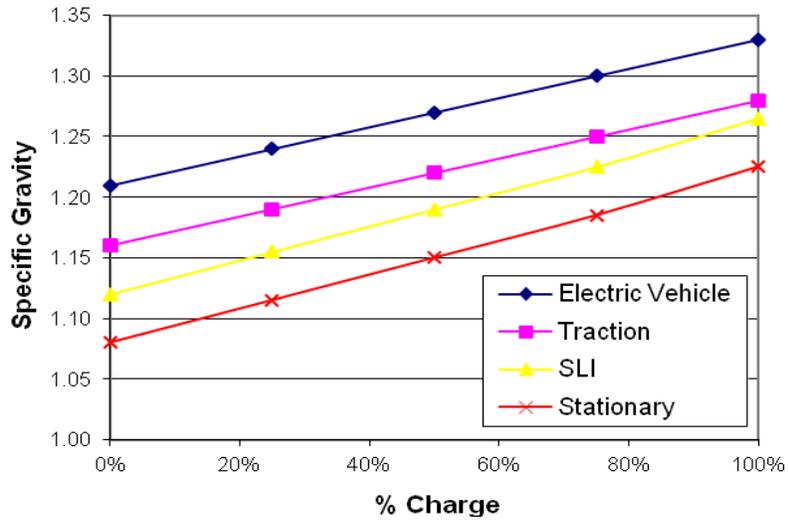
This paper describes how the relationship of the refractive index of H<sub>2</sub>SO<sub>4</sub> solutions to the specific gravity or relative concentration can be used to determine state-of-charge. The technique requires the development of a unique method of *in situ* measurement of refractive index and adapting it to practical battery measurements. The refractive index is a relative measure of the speed of light in a given medium and determines a number of optical properties such as how an optical wave propagates across a boundary. It is given by

$$n = c/v \tag{1}$$

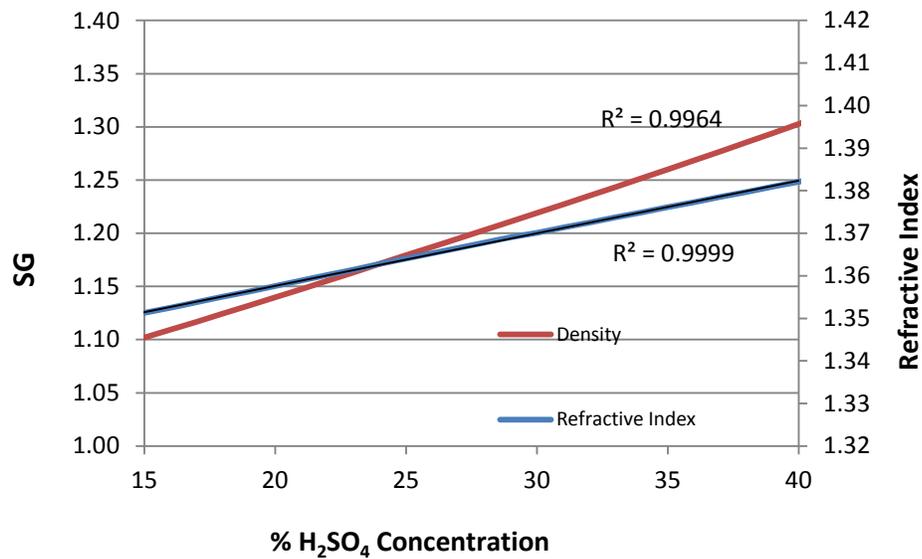
where  $v$  is the velocity of light within the medium and  $c$  the velocity of light. The index is always greater than 1 since nothing can exceed the speed of light in any medium. For example, Snell's law specifies the change in direction of a wave impinging on a boundary between two mediums of differing index and is a function of the individual indices. In terms of wave propagation in a waveguide, the index may determine the spatial mode of propagation and the losses.

Fig. 1 shows the typical relationship between SG and % SOC 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<sub>2</sub>SO<sub>4</sub> concentration. Over this typical range of SGs, the refractive index varies from about 1.36 to 1.38. Refractive indices for most materials are functions of temperature and the wavelength of light. In this case the indices are quoted for a temperature of 20°C and a wavelength of 589 nanometers.

## Battery Characteristics



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

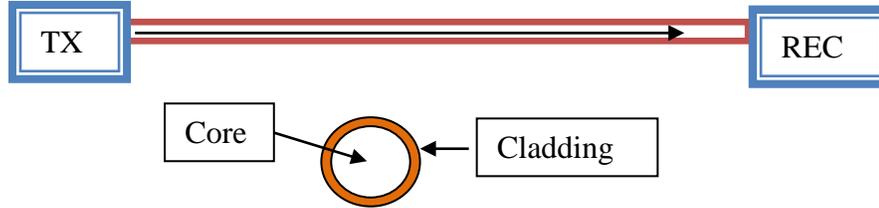


**Figure 2. The relationship between SG, electrolyte concentration and refractive index for a typical lead acid battery. R<sup>2</sup> = correlation values between the data and a straight line fit.**

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. This technology is well developed and is in widespread use to carry telephone calls over long distances.

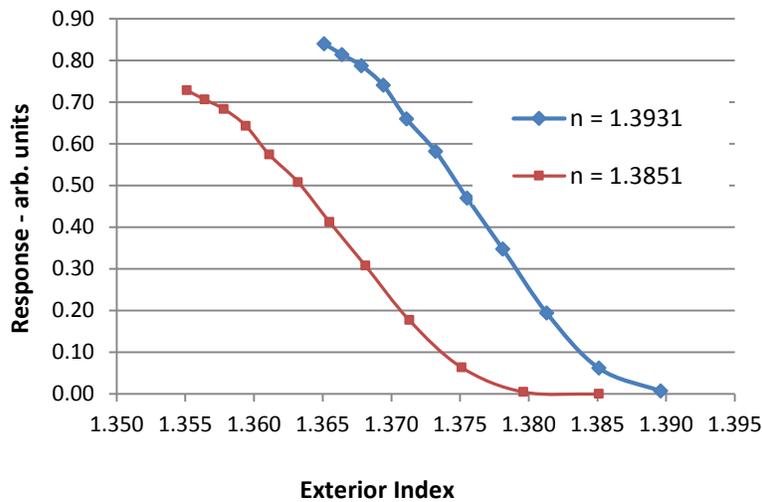


**Figure 3. Configuration of an optical fiber**

The condition for relatively lossless wave propagation inside such a device is given as:

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

where  $n_c$  is the refractive index of the core and  $n_{cl}$  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 a 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. 5 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 previously shown in Fig. 4.

It is also clear that as the liquid level of the enclosure changes so does the total response since the condition in Eq. 2 is violated over part of the tube. If the index of the electrolyte or the surrounding liquid doesn't change the configuration acts as a liquid "level" sensor. Unfortunately, in a battery it is impossible to completely separate these two effects. More specifically, we can approximately characterize the response of the sensor as:

$$I = I_0 \exp(-K(n_c^2 - n_{cl}^2)l) \tag{3}$$

Where  $I$  and  $I_0$  are output and input intensities of the optical signal,  $l$  is the active length of the sensor in the medium and  $K$  a constant. Level sensing using this method will be shown in a subsequent section.

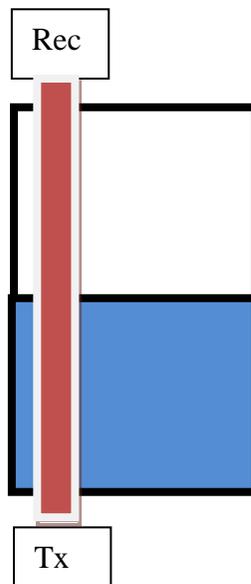
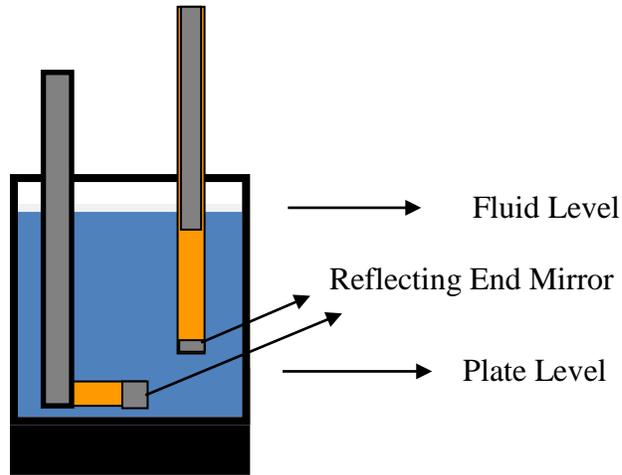


Figure 5. Example refractometer configuration in battery cell

The configuration shown in Fig. 5 is not practical and so we must resort to another configuration that is independent of electrolyte level. Consider the configuration shown in Fig 6a,b. The straight-through configuration is replaced with a tube containing an end mirror so the light that is transmitted into the tube is reflected at the end, recollecting 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 level is removed.

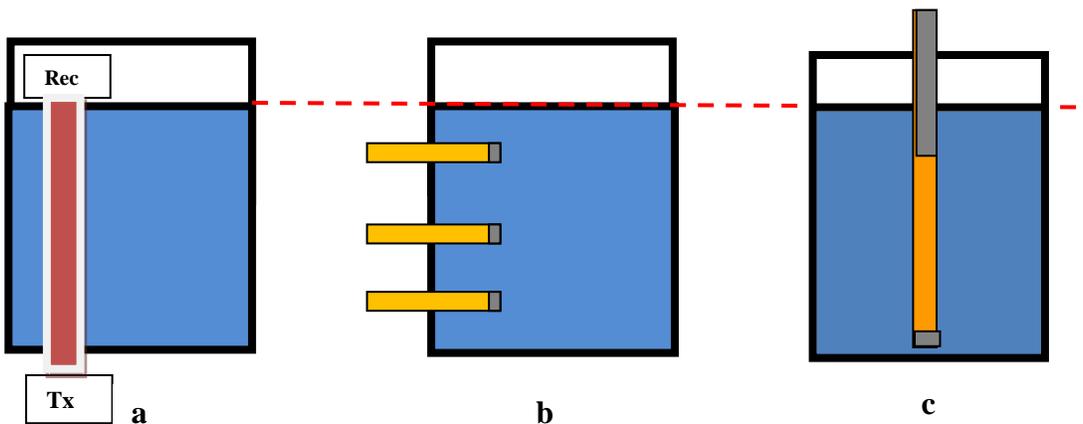


**Figure 6. Practical refractometer configuration in a battery cell a) vertical b) L shaped configuration for less electrolyte level sensitivity**

This is 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. The L shaped configuration shown in Fig. 6b is less sensitive to liquid level, somewhat more complex and more sensitive to charge stratification. Two additional topics of interest are temperature dependence and level sensing.

### Charge Stratification

One of the more vexing problems in battery management is charge stratification whereby the charge density  $q(x)$  is a function of electrolyte level. There are 3 potential ways of dealing with this problem shown in Fig. 7 below.



**Figure 7. Refractometer configurations to measure charge stratification a) in-line b) sampling c) reflecting. The plate level is shown by the dotted red line**

The in-line method is by far the simplest but required installation in the battery at production. The sampling method required inserting the sensor at various vertical positions after production and the third is the top entry with a separate access port. The total charge can be written as:

$$Q = K \int_0^d q(x) dx \tag{4}$$

where K is some constant. The function  $q(x)$  is not known but the sensor has the effect of integrating over the active total length immersed within the electrolyte.

### Temperature Dependence

Since density is both temperature and SOC dependent, corrections are required when measuring at a temperature different from the reference temperature as shown in Fig 8.

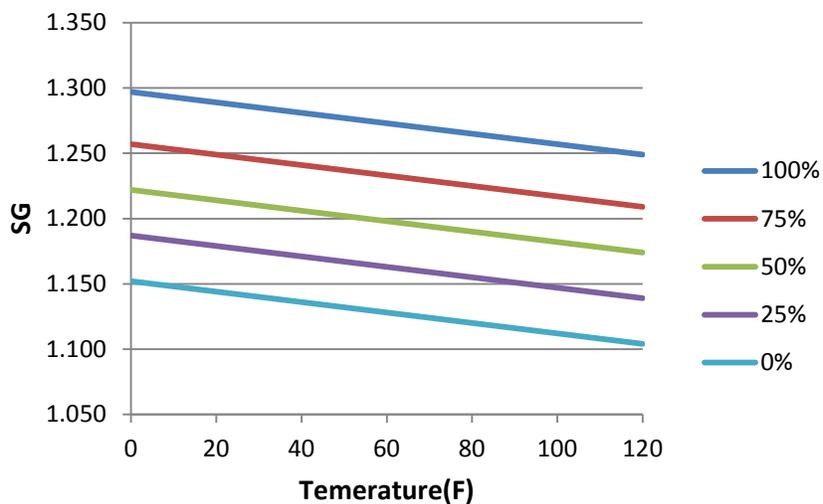


Figure 8. SOC Sensor temperature correction curves as a function of SOC and temperature

Eq. 5 yields the approximate SG as a function of SOC and temperature.

$$SG(T, \%SOC) = 1.15 + .0015(\%SOC) - 4.16 \times 10^{-4} T(F) \tag{5}$$

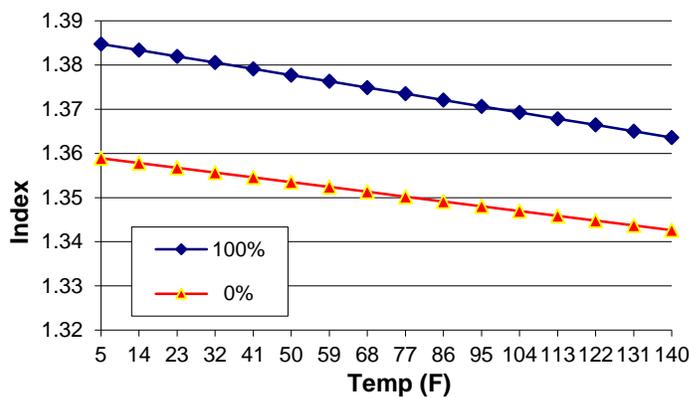


Figure 9. Refractive index variation as a function of temperature

Correspondingly the range of refractive indices corresponding to 0 and 100% SOC are shown in Fig.9. Charge levels of 0% and 100% correspond to H<sub>2</sub>SO<sub>4</sub> concentrations of 15 and 35% respectively. An approximate expression for **n** as a function of SOC and temperature is shown in Eq. 6.

$$n(T, \%SOC) = 1.3382 + 2.92 \times 10^{-4} \%SOC + 1.481 \times 10^{-4} T(F) \quad (6)$$

So to accommodate the range of expected indices as a function of SOC and temperature requires a refractometer with a sensitivity range of 1.34 to 1.39 corresponding to an SG of 1.1 to 1.35. Further to accommodate the temperature dependent effect of the refractive index as in a density reading, the electrolyte temperature must be known and corrected for. This can be accommodated by the insertion of a thermocouple in the probe. It is noted that for an electrolyte with a given index, the change in refractive index could be used to measure temperature.

### Calibration

Calibration of the sensor is accomplished via a secondary transfer process. The sensor output in volts corresponds to an index of refraction of the calibration liquid through the transfer function of the electronics. 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 referenced to the appropriate electrolyte SG via H<sub>2</sub>SO<sub>4</sub> references tables. Typical calibration data for an end reflecting sensor is shown in Fig. 10.

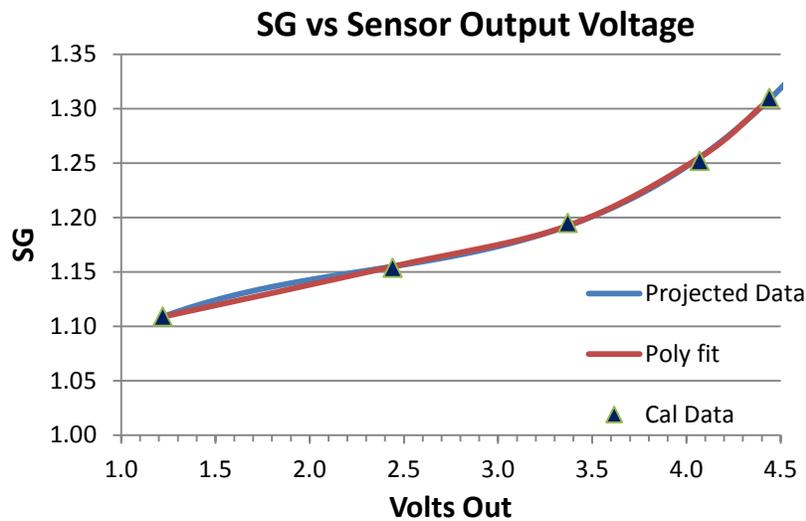
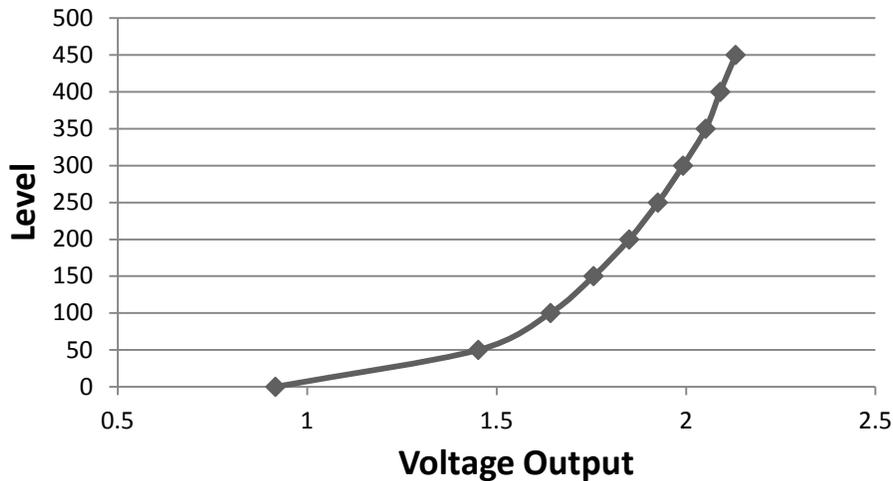


Figure 10. SOC sensor typical calibration curve

It is notable that the dynamic range of this sensor configuration is of the order 100 volts per unit refractive index.

### 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.

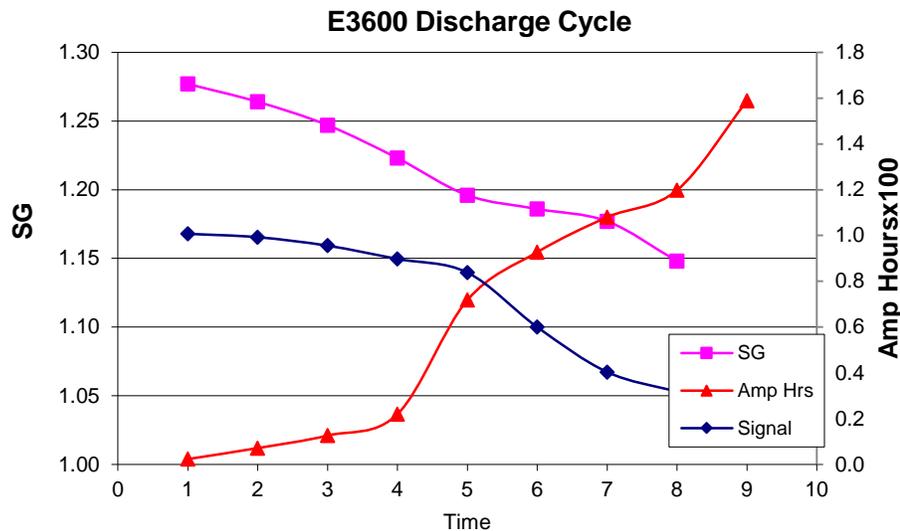


**Figure 11. SOC Sensor configured as a level sensor**

This is accomplished by changing the internal medium in the tube such that it is insensitive to refractive index variations. Output voltage of this configuration is shown in Fig 11. The physics of how and why this works is beyond the scope of this paper.

### Battery Test Results

Data in Figs. 12 and 13 were taken with an Exide E3600 6 volt battery (rated at 200 AH @ 20 hr) during charge and discharge cycles. The time intervals on the x axis of the chart are not equidistant. Further, during this experiment SOC was computed based on a linear calibration of the sensor. The voltage at maximum SOC was used to calculate the relative state of charge. No compensation for temperature was applied nor was any non-linearity accounted for.



**Figure 12. SOC measurements on an E3600 discharge cycle**

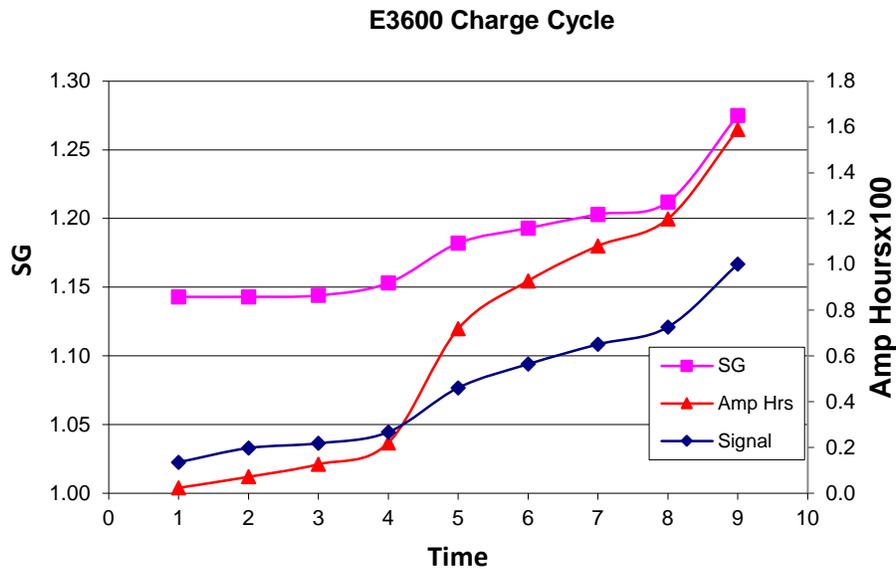


Figure 13. SOC measurements on an E3600 charge cycle

## Working Models

Fig. 14a,b shows working prototypes of the end reflecting configuration and as installed in a Surette S530 battery

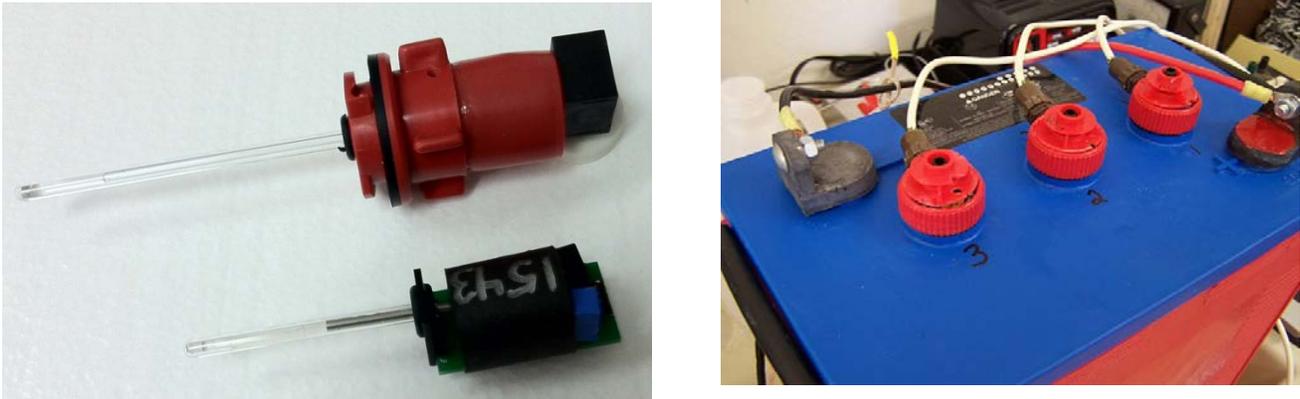


Figure 14. Prototypes of the end reflecting configuration a) battery cap packaged and OEM prototypes and b) earlier prototypes as installed in a Surette S530 battery

## Summary

In summary the optical method of state-of-charge determination appears to provide a viable new approach to state-of-charge sensing for open port lead-acid batteries. Eliminating the need for fluid extraction from the cell, this approach provides a rapid, real time capability for SOC determination.

## References

1. US Patent 6,356,675, *Fiber Optic Refractive Index Monitor*