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TECHNOLOGY BRIEF

Trending Multi-Frequency Impedance Data to Ensure Battery Reliability

ABSTRACT

Using examples taken from the field, this paper will show how modern test equipment can be used to measure and interpret changes over time in lead-acid battery characteristics. Because the trending of multi-frequency impedance characteristics can provide leading indicators of battery deterioration, corrective action does not necessarily involve cell replacement. In one case, impedance trends observed on a 60-cell string identified a few cells that were approaching critical levels of sulfation. An equalization procedure was recommended and a quarterly monitoring program was implemented. Over the next six months, impedance trends indicated improvements in health, not only for the most affected cells but for almost every cell in the string. In contrast, some cells within a string that received no corrective action showed progressive deterioration.

Effective management of a battery installation requires timely information about the condition of each battery unit (cell or monoblock) within the installation. To satisfy this requirement, Global Energy Innovations (GEI®) has developed the hand-held EC-Series™ Analyzers, which measure electrochemical impedance characteristics of a battery over a range of AC frequencies. The measurements are processed by Global Energy Innovations' CELScan® (Chemical Electrical Layer Scanning) algorithms to provide information not only about which battery units are approaching failure but also about the nature of those failures.

INTRODUCTION

All cells are not created equal and this fact has major consequences for the reliability of batteries. In particular, the useful life of a battery or string cannot be projected simply on the basis of typical cell data because interactions among the cells during operation will inevitably shorten the life of all of them. For the same reason, no single set of test results can reveal cells that are aging abnormally. Only by analyzing trends in test results over a period of months or years is it possible to identify components (cells, monoblocs or interconnections) that may require attention.

Cell performance charts published by battery suppliers are usually presented as "typical" and the user is cautioned that practical results may differ greatly, depending on operating conditions and other factors. One factor rarely addressed by the suppliers is the intrinsic variability of battery cells. At best, the useful life of a multi-cell battery (or battery string) can never exceed that of its weakest cell and actual battery life can be even shorter[i]. Strong cells wear out more rapidly because they must work harder to compensate for weaker cells, while weak cells get overstressed with each charge and discharge cycle, degrading them even faster. Furthermore, the difference between published and actual life expectancy increases with the spread in individual cell characteristics[ii]. Indeed, regularly monitoring the extent of this spread provides vital information about the health of a battery string. On the other hand, an operating plan that relies primarily on “typical” life curves will almost certainly lead to premature (and potentially catastrophic) system failures.

According to IEEE (The Institute of Electrical and Electronics Engineers), the only sure way to assess the health of a multi-cell battery is to perform regular capacity tests on every cell. However, because it is rarely feasible to perform capacity tests more often than once every 1-5 years, IEEE recognizes the value of alternative inspection methods that can be performed at shorter intervals, stating in part that[iii]:

- Internal ohmic measurements can be used to evaluate the electrochemical characteristics of battery cells. They may provide possible indications of battery cell problems and may identify those cells having internal degradation.
- Ohmic measurements can be used as a trending tool to identify cells that may require further evaluation. When significant changes from the baseline occur, capacity testing should be used to verify whether identified cells are in fact defective.

EQUIPMENT METHODS

In the past, the manual tasks of measuring, recording and analyzing battery characteristics on a routine basis could be costly and tedious. Fortunately, hand-held test equipment is now available that can streamline these tasks and greatly relieve the tedium of performing them. Results presented in this paper were obtained with Global Energy Innovations' EC-Series Analyzer™ (EC2000)™, a hand-held instrument that provides the added capability of multi-frequency impedance analysis. This capability exploits the principles of Electrochemical Impedance Spectroscopy (EIS)[1], a technique that has previously found widespread use only in the laboratory. Even though EIS has long been an important tool for electrochemical research, its underlying principles may be unfamiliar to many readers. For those readers, the following summary is offered as a brief introduction to the subject. More complete information may be found in the references listed at the end of the paper.

BATTER APPLICATIONS OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The application of EIS to batteries is far from new but until recently, the size and cost of the test equipment, coupled with the complexity of data analysis has largely restricted its use to the research laboratory. For the same reasons, most of the early research on battery impedance focused on the characteristics of individual electrodes rather than of complete cells[iv]. One paper that bridged the gap between research and application was published by IEEE in 1991[v]. In that paper, Pye and Golestaneh monitored the complex impedance characteristics of a lead acid cell at intervals during the course of accelerated aging. The impedance measurements covered an AC frequency range from 4 to 1000Hz. Each set of impedance data was fitted mathematically to the equivalent circuit shown in **Figure 1**.

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[1] Also known as Frequency Response Analysis or FRA.

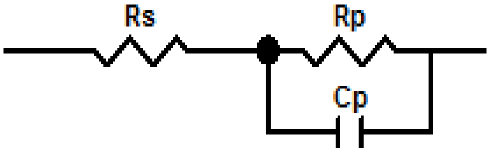


Figure 1. Three-element equivalent circuit.

The series resistor Rs is a lumped quantity that includes both the electronic resistance of metal components of the cell and the ionic resistance of the acid. The parallel combination Rp and Cp represents the electrochemical characteristics of an electrode-solution interface: Rp ("the charge transfer resistance") accounts for energy consumed in transferring electric charge across the interface and Cp (the "double layer capacitance") accounts for the capacitor-like behavior of the interface. The results indicated that Rs was a good indicator of the state of charge but was relatively insensitive to changes in cell health. In contrast, the values of Rp and Cp both changed appreciably as the cell wore out.

Since that time, a number of excellent publications have appeared that expand and explain these observations[vi]. In particular, it is now clear that correlations observed between cell health and electrochemical parameters such as Rp and Cp arise from the fact that they all depend on the interfacial area between the electrode-active material and the electrolyte. For example, the capacitance **C** of a parallel plate capacitor is directly proportional to the plate area **A**:

$$\mathbf{C=\varepsilon A/4\pi d}$$

Where ε is the dielectric constant and **d** is the plate separation. In the case of a double layer capacitor, **A** represents the contact area between the electrolyte and the active material of the electrode. As a battery wears out, the loss (or passivation) of active material is manifested as a decrease in the charge storage capacity. However, at the same time, it produces a corresponding reduction in the double layer capacitance. An analogous explanation exists for the correlation between capacity and charge transfer resistance.

A convenient way to analyze the relationship between the condition of a cell and its impedance response involves the complex-plane representation (also known as a Nyquist or Cole-Cole plot) illustrated in **Figure 2**.

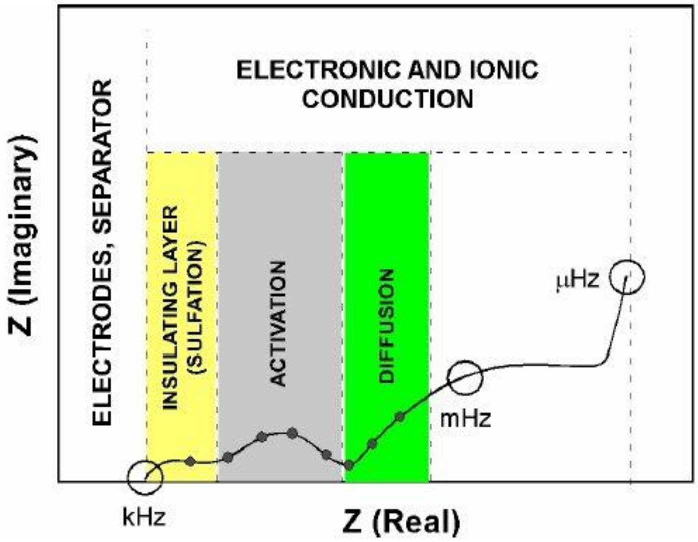


Figure 2. Typical complex-plane plot for a lead acid battery.

In these plots, each data point corresponds to a single AC frequency and its X- and Y-coordinates represent the real and imaginary components of the measured impedance at that frequency. As shown in **Figure 2**, the AC frequencies may range from kilohertz (kHz) down to microhertz (µHz).

At the highest frequencies, the impedance is controlled by electron movements in metallic components and resistive films. As the frequency is lowered (moving from left to right in the figure), a sequence of other processes becomes important including ionic migration, the electrostatic charging of electric double layers, and charge transfer reactions at electrode surfaces. At frequencies in the millihertz (mHz) range and below, diffusion processes in liquid and solid phases tend to dominate. Obtaining data in this low frequency range is impractical outside the laboratory because it would require many minutes per data point. For example, 1mHz corresponds to 1 cycle every thousand seconds. In the case of the lead-acid battery, diagnostic information about the negative electrode can be obtained at frequencies above 1 Hz, allowing each measurement to be completed in just a few seconds. However, corresponding information about the positive electrode would require data at substantially lower frequencies. Because the resulting measurement times would be too long for field applications, we limit data collection to a frequency range appropriate for the negative electrode. Fortunately, as explained in the next section, this limitation has little impact on the end results.

DATA ANALYSIS

As indicated above, multi-frequency impedance measurements on a battery can yield parametric information that is directly related to significant battery characteristics. The parameters may be equivalent circuit elements of the type shown in **Figure 1** or they may be real and imaginary coordinates in the complex impedance plane shown in **Figure 2**. Regardless of the parameters chosen, the first step in converting them to useful information is to develop calibration equations that relate the parameters to one or more battery characteristics.

The characteristics of interest will vary from one application to another and suitable equations will need to be developed accordingly. For example, a key characteristic of automotive batteries is their ability to start an engine on a cold morning. For this application, suitable calibration equations could be developed by collecting impedance parameters on a series of batteries of known CCA ratings.

To date, Global Energy Innovations has focused primarily on applications where the characteristic of primary concern is the battery's ability to deliver charge at a required rate for a required time. Hence, we developed calibration equations by performing parallel impedance and load tests on batteries as they underwent accelerated aging procedures. We found that batteries of different types and sizes yielded calibration equations with somewhat different coefficients and have since devised empirical methods for adjusting the coefficients to allow for these differences.

To obtain quantitative estimates of cell capacities for battery strings that have been in service for more than a few months, the calibration equations must be adjusted with impedance data recorded on fresh cells of the same type. In practice, fresh cell are rarely available, especially for strings that have been operating for several years. In such cases, we derive an empirical baseline capacity value for the string and use that value to obtain relative estimates of individual cell capacities. While less than ideal, even relative information about the spread of cell capacities in a string can be very helpful in avoiding premature failures. Field test results that illustrate this point are presented later in the paper.

In the previous section, it was mentioned that our impedance measurements yield no direct information about the condition of the positive electrode. Fortunately, this limitation does not affect the reliability of capacity values estimated from impedance data. The reason is quite simple: any change in the battery that lowers its capacity would prevent complete charging of the negative electrode. Consequently, the complex impedance of the battery, being controlled primarily by the negative electrode, would still register the loss of capacity. In other words, the negative electrode will appear to be sulfated, even though the sulfate crystals may be identical with those formed during battery discharge.

It is for this reason that we label the capacity loss in a flooded cell as "Sulfation". In effect, we are using the term as a symptom of capacity loss, rather than a diagnosis of the root cause.

FIELD TESTS

Summary charts for one set of tests on a string of flooded lead-acid cells appear in **Figure 3**.

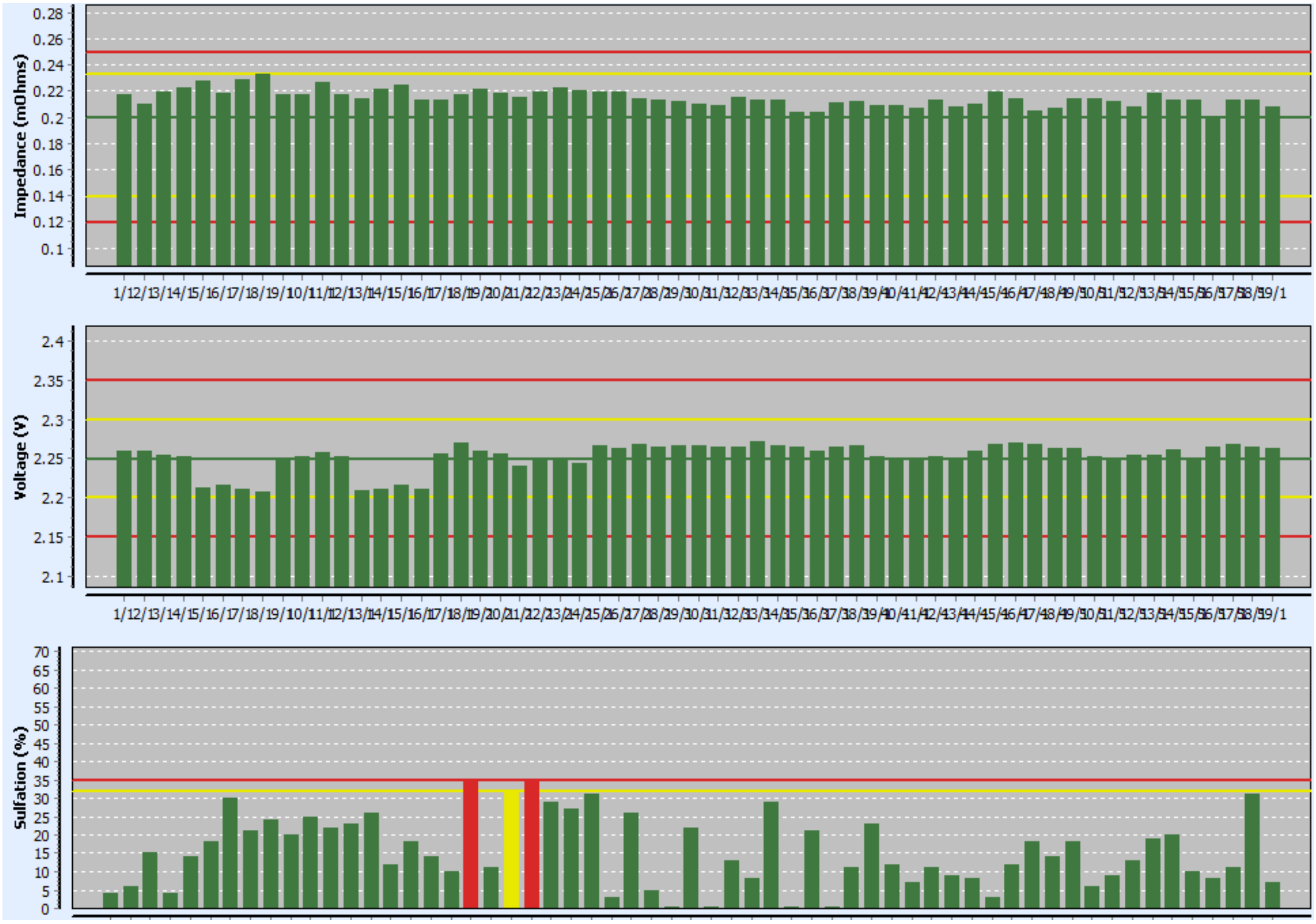
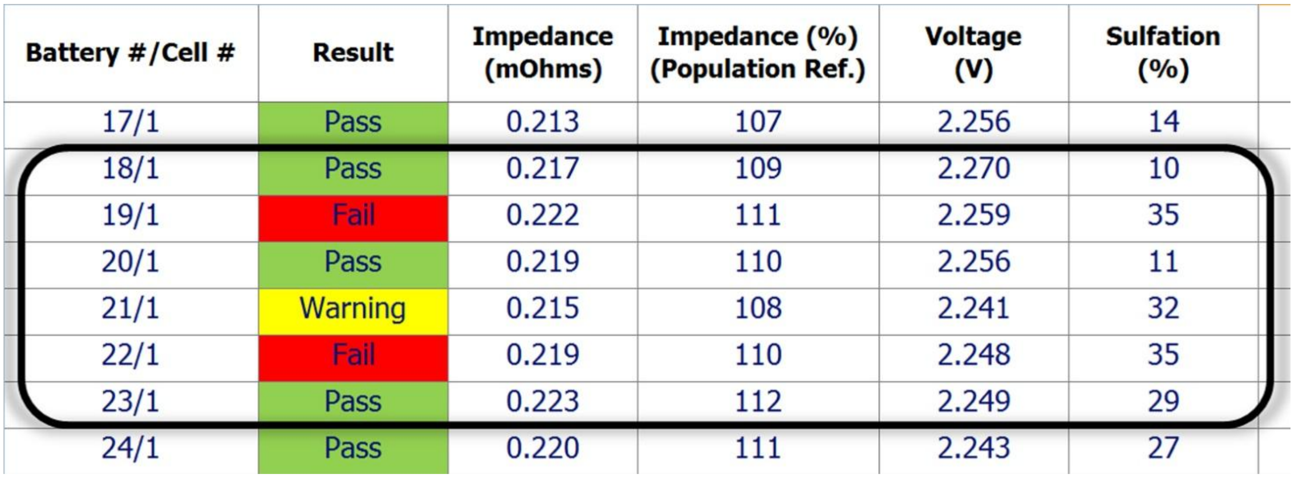


Figure 3. Computer-generated summary charts for typical test results on a string of flooded lead-acid cells.

The yellow and red lines in these charts represent “Warning” and “Fail” levels that were chosen by the operator. It is immediately apparent from these charts that, while most of the cells were operating within acceptable limits, there were several cells that required attention. Note that none of the cells in this string were flagged as abnormal by either of the conventional measurements of float voltage or (single-frequency) impedance. The only indicator that detected abnormal cells in this string was the relative sulfation level.

The following case studies show how the trending of multi-frequency impedance data can reveal out-of-family battery cells well before they fail and also provide feedback on the effects of corrective action. The results were collected during routine tests that were conducted on strings of flooded lead acid cells at approximately quarterly intervals. Because no record was available of cell characteristics at the time of installation, algorithms built in to the instrument were applied during the first test to establish a string baseline for each parameter. Results obtained during subsequent tests were then compared with those baseline values.

Figure 4 illustrates a portion of the computer-generated data table that corresponds to Figure 3.



Battery #/Cell #	Result	Impedance (mOhms)	Impedance (%) (Population Ref.)	Voltage (V)	Sulfation (%)
17/1	Pass	0.213	107	2.256	14
18/1	Pass	0.217	109	2.270	10
19/1	Fail	0.222	111	2.259	35
20/1	Pass	0.219	110	2.256	11
21/1	Warning	0.215	108	2.241	32
22/1	Fail	0.219	110	2.248	35
23/1	Pass	0.223	112	2.249	29
24/1	Pass	0.220	111	2.243	27

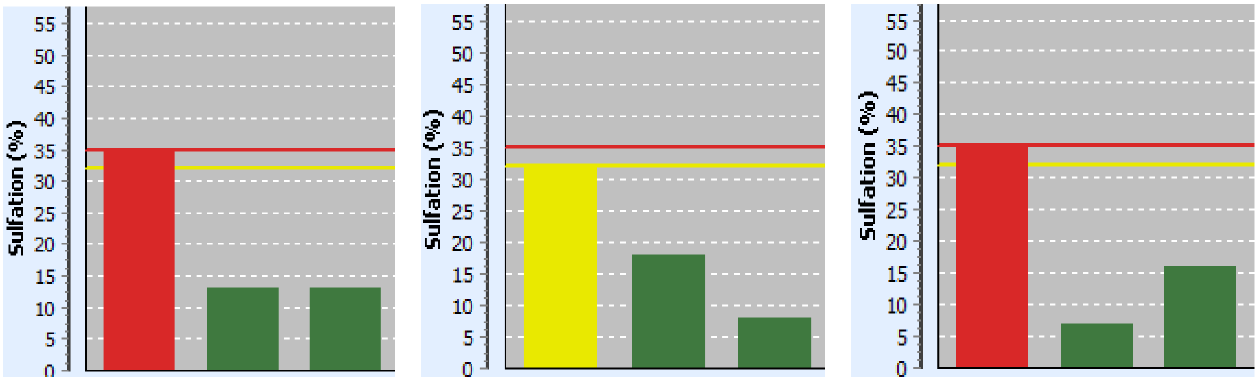
Figure 4. Partial data table obtained in the summer of 2012 on a group of cells in "String A".

Based on the abnormalities apparent from **Figures 3** and **4**, a program of regular equalization procedures was recommended. Data collected on the same cells six months later are shown in **Figure 5**.

Battery #/Cell #	Result	Impedance (mOhms)	Impedance (%) (Population Ref.)	Voltage (V)	Sulfation (%)
17/1	Pass	0.180	90	2.252	13
18/1	Pass	0.196	98	2.265	11
19/1	Pass	0.196	98	2.254	13
20/1	Pass	0.193	97	2.250	0
21/1	Pass	0.196	98	2.236	8
22/1	Pass	0.197	99	2.242	16
23/1	Pass	0.194	98	2.242	5
24/1	Pass	0.196	98	2.237	0

Figure 5. Data table obtained early in 2013 on the same "String A" cells as those in **Figure 4**.

Comparison of **Figures 4** and **5** shows that equalization successfully lowered the sulfation levels of all three abnormal cells. To see how these cells fared over time, we generated "cell history" bar charts of the individual sulfation parameters over a six-month period. Results for four of the cells highlighted above appear in **Figure 6**.



Cell 19 **Cell 21** **Cell 22**

Figure 6. Trends in the relative sulfation levels of selected cells in String A over a six month period.

For each cell in **Figure 6**, the sulfation levels decreased substantially following an equalization procedure and remained within acceptable limits for both of the subsequent tests. Summary data over the same six month period for all cells in String A appear in **Figures 7-9**.

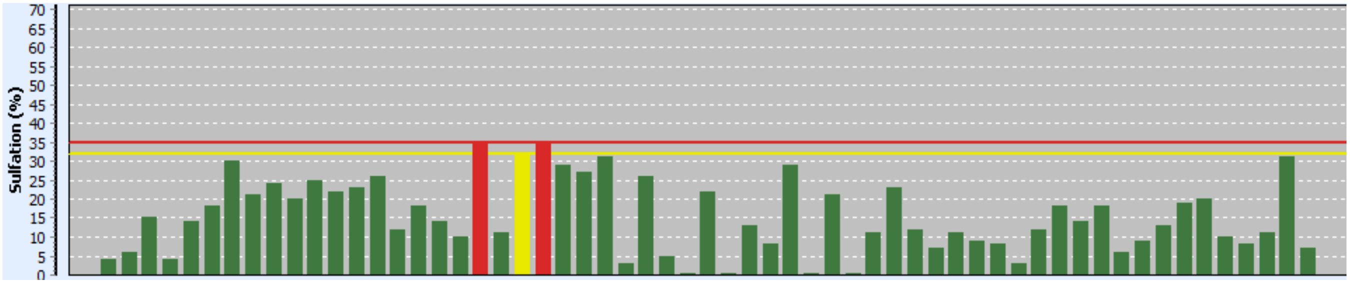


Figure 7. Relative sulfation levels of String A cells in the summer of 2012.

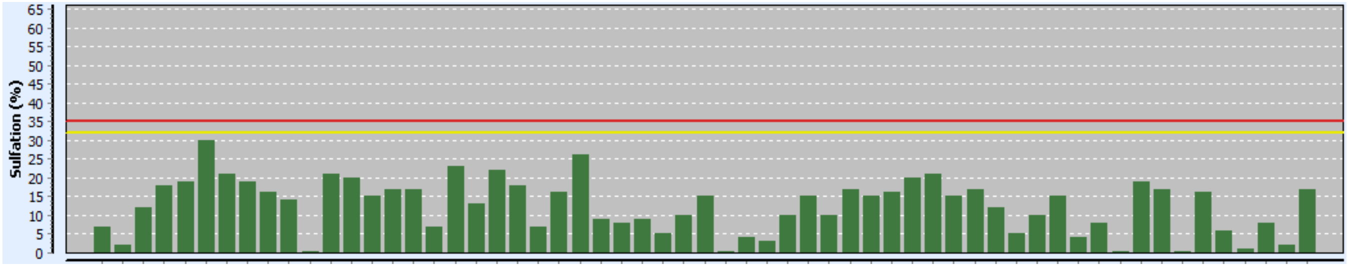


Figure 8. Relative sulfation levels of String A cells in the fall of 2012.

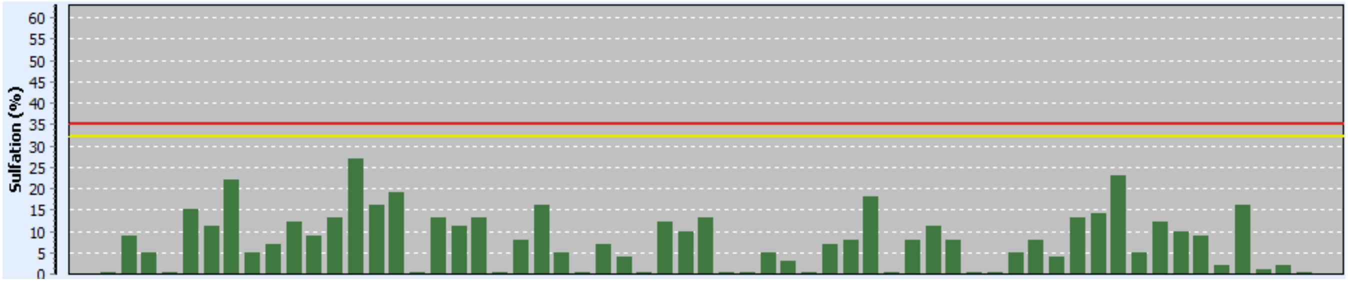


Figure 9. Relative sulfation levels of String A cells early in 2013.

Taken together, these results clearly demonstrate that virtually all cells in String A derived significant benefit from the equalization procedure. However, as shown in **Figures 10-11**, very different trends were observed on a string of 120 cells that did not receive an equalization procedure.

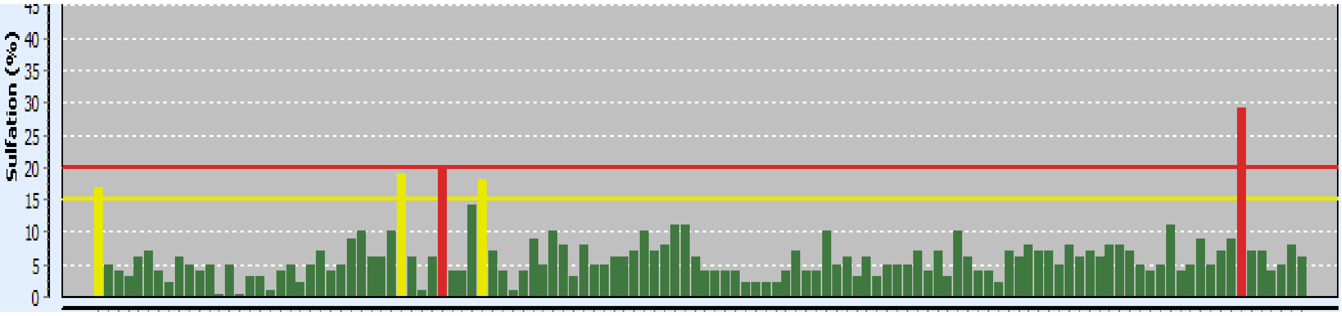


Figure 10. Relative sulfation levels of String B cells in the fall of 2012.

When tested in the fall of 2012, the vast majority of String B cells showed relative sulfation levels below 15% and only one of them approached the 30% level chosen as the “fail” criterion for String A. For this reason, higher priority was apparently given to corrective maintenance on String A.

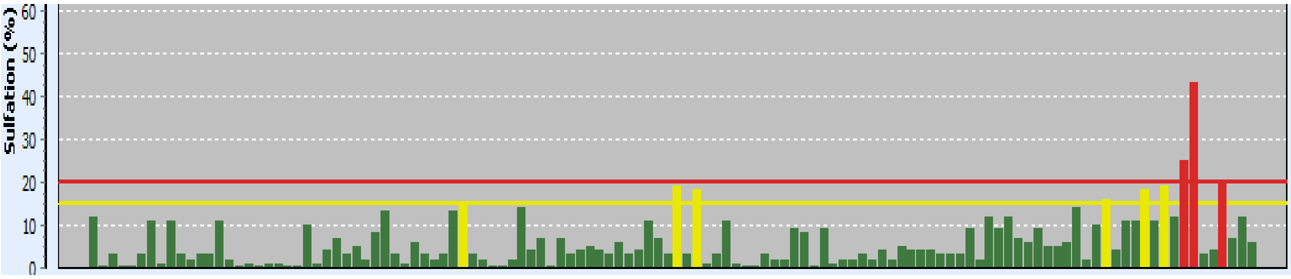
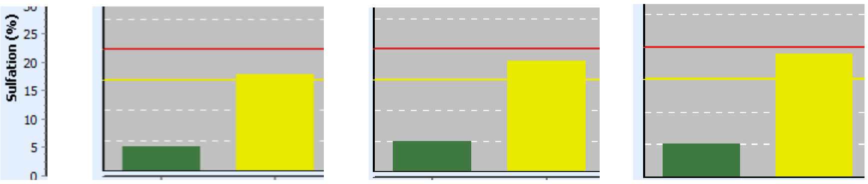


Figure 11 - Relative sulfation levels of String B cells in Early 2013.

When tested three months later, the relative sulfation levels had increased substantially on a group of cells at the upper end of String B. Trends observed over three months on cells within that group are shown in **Figure 12**. The changes clearly warranted immediate corrective action and strong recommendations were made to that effect.



Cell 105 **Cell 109** **Cell 111**

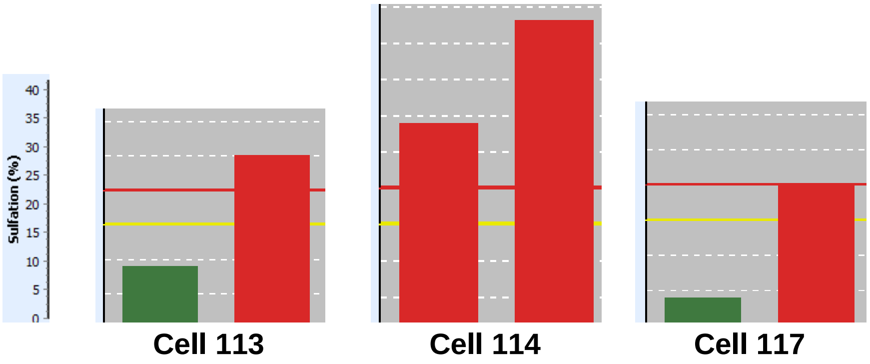


Figure 12. Trends in the relative sulfation levels of selected cells in String B over a three month period.

CONVLUSIONS

Analysis of results taken directly from field tests shows that:

- A maintenance scheme that includes regular monitoring of battery characteristics is the only way to ensure the reliability of backup or standby power systems.
- Microprocessor-based battery testers in combination with intelligent battery management software can greatly relieve the tedium of systematic data collection and analysis.
- The trending of multi-frequency impedance data on lead-acid batteries can reveal not only which cells need attention but also how well they respond to corrective actions.

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[i] http://www.mpoweruk.com/balancing.htm

[ii] http://www.mpoweruk.com/reliability.htm

[iii] Annex J, IEEE Standard 450-2010 - IEEE Recommended Practice for Maintenance, Testing, and Replacement of Vented Lead-Acid Batteries for Stationary Applications

[iv] See for example, Solartron Technote 31: "Electrochemical Impedance Spectroscopy (EIS) for Battery Research and Development", http://www.solartronanalytical.com/Literature/Technical-Notes.aspx

[v] E. L. Pye and K. Golestaneh, "Impedance spectroscopy and battery quality with cycle-life", Proc. 6th Annual Battery Conference on Applications and Advances, 1991, 111-122.

[vi] See, for example, J.M. Hawkins, L.O. Barling, "Some aspects of battery impedance characteristics", Seventeenth International Telecommunications Energy Conference, INTELEC '95;
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