

# Individual Cell Voltage Variation during Float Charge in Lead-Calcium Batteries

M. S. (Steve) Clark P.E.  
Senior Engineer  
Bechtel Nuclear, Security and Environmental  
Knoxville, TN 37922

## Abstract

The principal vented-lead-acid battery (VLA) technology manufactured in the United States is lead-calcium. Worldwide the principal valve-regulated-lead-acid (VRLA) battery technology is lead-calcium. Calcium is added as a hardener to the positive and negative grids. The use of calcium produces a battery with excellent float characteristics and very low gassing, but there are tradeoffs. One of these is the lack of uniformity in individual cell voltages during float charge. In some instances, this has led to user's installing Individual Cell Equalizing (ICE) devices.

The purpose of this paper is to examine individual cell voltage (ICV) variation in both vented and valve-regulated batteries using lead-calcium technology. It will look at industry data comparing float ICV to battery capacity, Tafel curves/lines, plate polarization, the use of depolarizing agents, and look at real world data on severe ICV variation.

## Introduction

One of the first tasks usually assigned to a new battery engineer is to review test results. Nearly always these include individual cell voltage (ICV) readings. Most often the acceptance criteria were established by a predecessor, the battery manufacturer, regulating body etc. and the new engineer often follows them without understanding how they were established.

Most acceptance criteria focus on the minimum ICV during float charge and even then do not provide the information on how they were established. In most cases, there is no discussion or information on high voltage cells. This is a legacy from the days of lead-antimony where there is almost no variation in ICV during float charge. Since adoption of lead-calcium in the 1950's there has been much discussion on ICV variation during float charge and there are several papers on the subject<sup>2,3</sup>. However as we experience turnover in our industry, the question of what is an acceptable float voltage continues to be raised.

With the introduction of the lead-calcium Valve Regulated Lead Acid (VRLA) battery, the situation has only gotten worse because ICV variation is often much greater for VRLA batteries.

## Battery Aging

Before launching into the discussion of cell voltage variation, it is important to understand why so much attention is paid to battery and cell voltage.

In a lead-acid battery, the primary failure mode is positive grid corrosion. Controlling the rate of corrosion is central to maximizing battery life. Factors like: grid thickness and composition and, for the purposes of this discussion specific gravity are beyond user control. The factors that users control are the operating temperature and the voltage.

As we know, as battery temperature goes up battery life goes down. The same is true if we operate the battery outside of the manufacturer's recommendations. If we operate the battery above the maximum recommended float voltage we increase the over voltage on the positive plate (known as polarization) which increases the grid corrosion rate. For a VRLA battery we also increase the gassing rate which leads to dry out and capacity loss. This is the reason there are voltage and time limits associated with freshening and equalizing charges for both VLA and VRLA batteries.

The effect of temperature on the battery is very similar. However in this case, increasing temperature results in increased float current. The increase in float current increases the rate of grid corrosion. This is why manufacturers recommend that at elevated operating temperatures the battery float voltage be adjusted down to reduce the float current. At low battery temperatures, the opposite is true. The reduced current caused by the low temperature may not be sufficient to overcome self-discharge.

Operation below the manufacturer's recommendations has the potential to reduce battery life as well. The optimum life of the positive plates is achieved with an over potential of 40 millivolts<sup>3</sup> (OCV+.04). However at 40 millivolts, the negative plates undergo self-discharge and frequent equalizing charges are required to maintain the battery fully charged. Operation below the 40 millivolt limit results in increased positive grid corrosion as voltage is reduced further, both the positive and negative plates begin self-discharge. If this condition is allowed to exist for a significant period of time, the sulfate crystals formed may be sufficiently large to prevent the battery/cell from being recharged.

The above provides an understanding of why ICV variation is a concern in battery systems.

## **Plate Polarization**

Plate polarization is simple to understand. It is the over voltage applied to the plate beyond the electrochemical potential. In a secondary battery, the over potential is applied to keep the battery in a fully charged state. The difficulty is in being able to measure the value directly. What we can measure is the voltage between the plates and the electrolyte using a reference electrode.

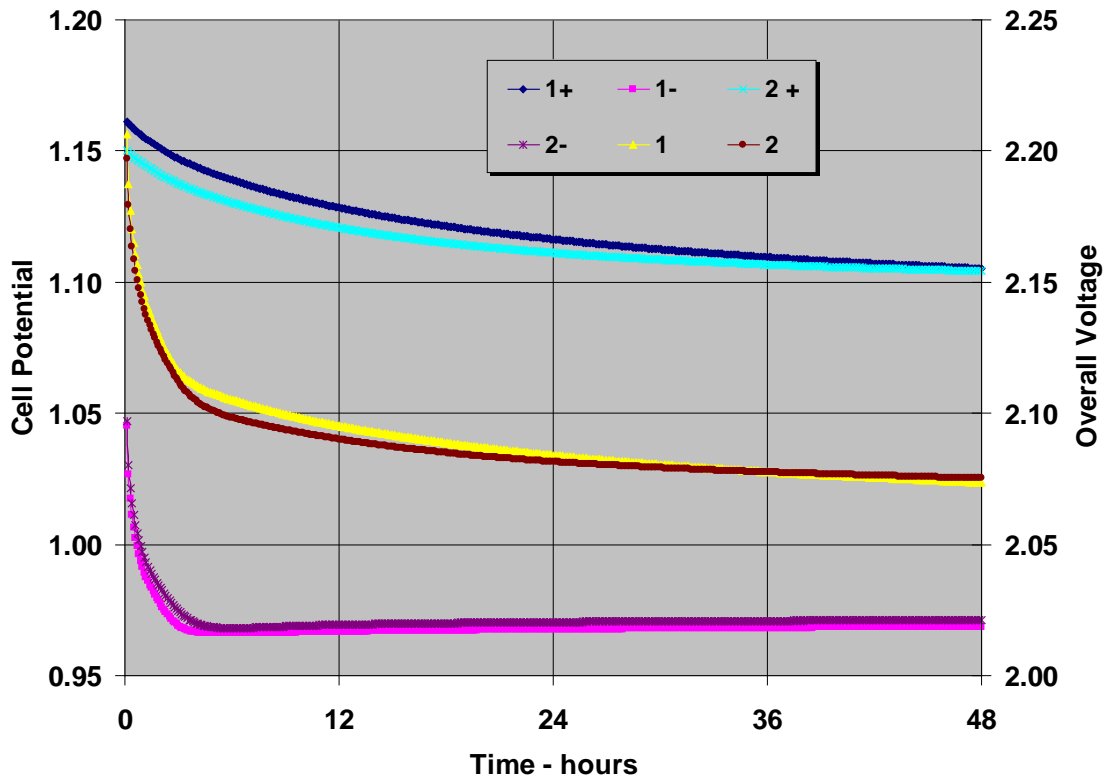
In a VLA battery, it is relatively simple to measure using a standard voltmeter and a Mercury/Mercurous Sulfate reference electrode which can be easily procured. The electrode is immersed in the electrolyte and the voltage is measured between the lead on the electrode and the battery post. The ICV is simply the sum of the individual plate voltages.

Since VRLA batteries are sealed, users do not normally use reference electrodes as a troubleshooting tool. To do so involves removing the vent cap which would result in loss of moisture from the cell. That is why it is not a normal practice and one generally reserved for specialists trained in doing so or in a laboratory.

It is important to understand that the voltages measured using a reference electrode are affected by the electrode materials and do not reflect the electrochemical potential of the plate materials. As an example, the lead dioxide in the positive plates in a lead acid battery have an electrochemical potential of 1.685V and the lead negative plates have an electrochemical potential of .356V for a total potential of 2.041<sup>4</sup> volts which does not account for the contribution of the electrolyte specific gravity.

When measured with a Mercury/Mercurous Sulfate reference electrode, the reading in a 1.215 S.G. cell (Figure 1), the readings are approximately positive plates: 1.105V and negative plates: .97V for an open circuit voltage of 2.07V.

**Open Circuit Stand Preceding Discharge  
(NLI Data)**



**Figure 1, Plate Polarization Stand Test**

When using a reference electrode to determine the cause of ICV variation, it is important to not get concerned with the impact of the reference electrode on the plate voltages. The important thing is what the voltages tell us. For installed batteries, reference electrode voltages are normally taken under float charge conditions. The important characteristic is that the positive plate voltages for the cells should show almost no variation. Positive plate voltages that are either too high or too low indicate a problem that must be addressed or the cell must be replaced.

If the positive plate voltages show minimal variation (typically less than .01vdc), then the negative plate polarization is the cause of the ICV variation. An example is shown in Figure 2.

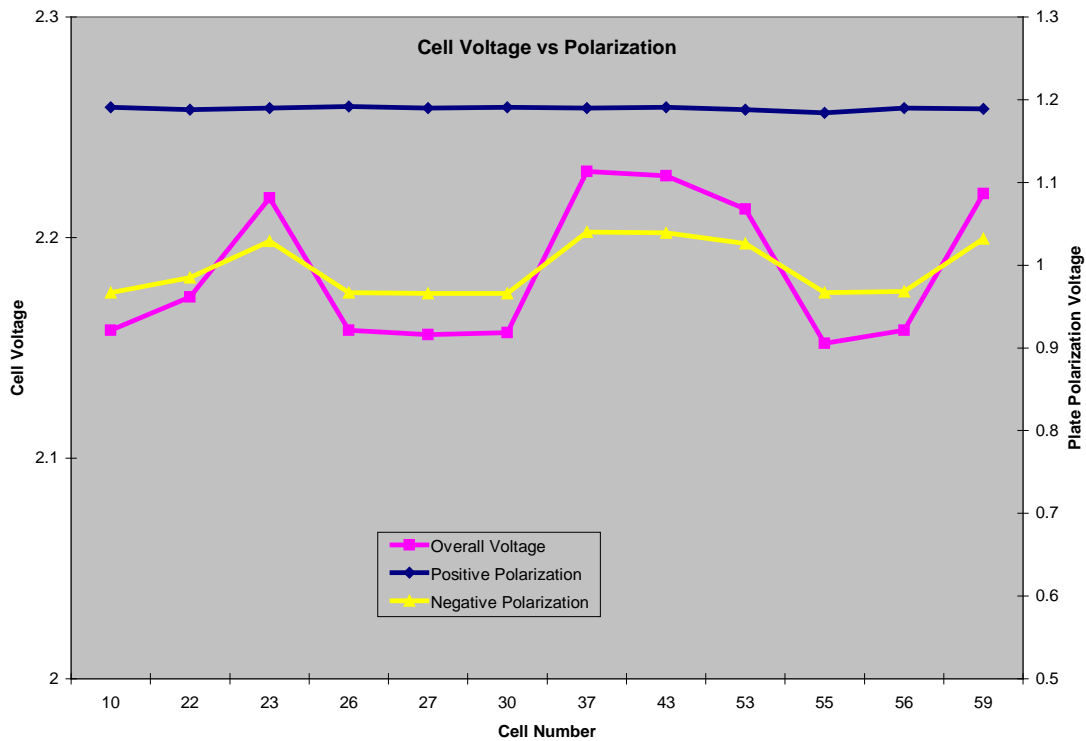


Figure 2, Example Plate Polarization and ICV Graph

### Minimum Float ICV Determination

Determining the nominal open circuit voltage (OCV) of a lead-acid cell is easily done using a correction factor. This is often referred to as a thumb rule. The correlation between acid concentration and open circuit voltage is documented in Table 39 of "Storage Batteries" <sup>4</sup>. As can be seen in Figure 3, the value of the correction factor/thumb rule varies with specific gravity but for most current lead-acid batteries, a good value is S.G. + .845.

In order to overcome the effects of self-discharge a potential above open circuit must be applied. A value of 60 millivolts is commonly used.

Using the 60 millivolt value provides the following Minimum ICV determination:

$$\text{Minimum Float ICV} = \text{OCV} + .06$$

$$\text{Example: S.G. of 1.250, Minimum Float ICV} = 1.250 + .845 + .06 = 2.155\text{V}$$

The 2.155V limit is for each individual cell in the battery. It is not used for setting the minimum battery float voltage. If we allow for a maximum variation of .04V below the average for the battery, then the minimum battery float voltage would be #cells X (2.195).

This is the theoretical minimum float voltage at the battery's design operating temperature. The battery manufacturer's recommendations should always be followed when establishing the minimum battery float voltage. It may also be necessary to adjust the voltage up for low operating temperatures and down for high operating temperatures.

<b>Figure 3, Specific Gravity Relationship to OCV and Calculated Correction Factor</b>		
<b>S.G.</b>	<b>Mean OCV (Note 1)</b>	<b>Correction Factor/Thumb Rule (Note 2)</b>
1.100	1.961	0.861
1.150	2.006	0.856
1.200	2.049	0.849
1.215	2.063	0.848
1.250	2.095	0.845
1.280	2.125	0.845
1.300	2.144	0.844

Figure 3 Notes:

1. The OCV data presented in Figure 3 is from Table 39 of Storage Batteries <sup>(4)</sup>, with the exception of the values for S.G. of 1.215 which were created using a linear interpolation of the correction factor values for 1.200 and 1.250.
2. Correction factors were calculated using the difference from the reported Mean OCV value by subtracting the S.G.

### Maximum Float ICV

Just as many of you, I've written battery specifications where the maximum allowed ICV voltage variation was +/-0.04vdc. This is, if you will, an industry standard, for vented lead-calcium batteries and is often misapplied to VRLA cells.

While it may seem like heresy to some, the use of a maximum +.04vdc variation requirement may be an area where we, as a user community, are causing battery prices to increase for no real gain in reliability or quality. The fundamental reason is that, based on natural variation in negative plate polarization, there is no real upper limit for float ICV. The actual limit comes into play, when the high voltage cells begin to starve the lower voltage cells of sufficient voltage to maintain them in a fully charged condition (i.e. the float ICV is less than the minimum required). When this occurs, an equalizing charge is normally applied to the battery.

Not all VRLA manufacturers recommend equalizing charges. Even those that do, provide strict criteria that must be followed because over equalizing a VRLA battery results in shortened battery life and/or battery damage.

### Tafel Curves

One of the questions that arises when discussing float ICV is how are the various parameters, positive plate polarization, negative plate polarization, float voltage and float current related? The answer is the Tafel curve for that particular battery type. Tafel Curves are produced by manufacturers. The best way to understand the curve is to start on the side that shows the applied average cell voltage (charger voltage divided by the number of cells). Reading across the curve, we can then determine the expected positive and negative polarization values along with the float current which is typically given in microamps/Ah and/or milliamps/100Ah. A typical Tafel curve is shown in Figure 4.

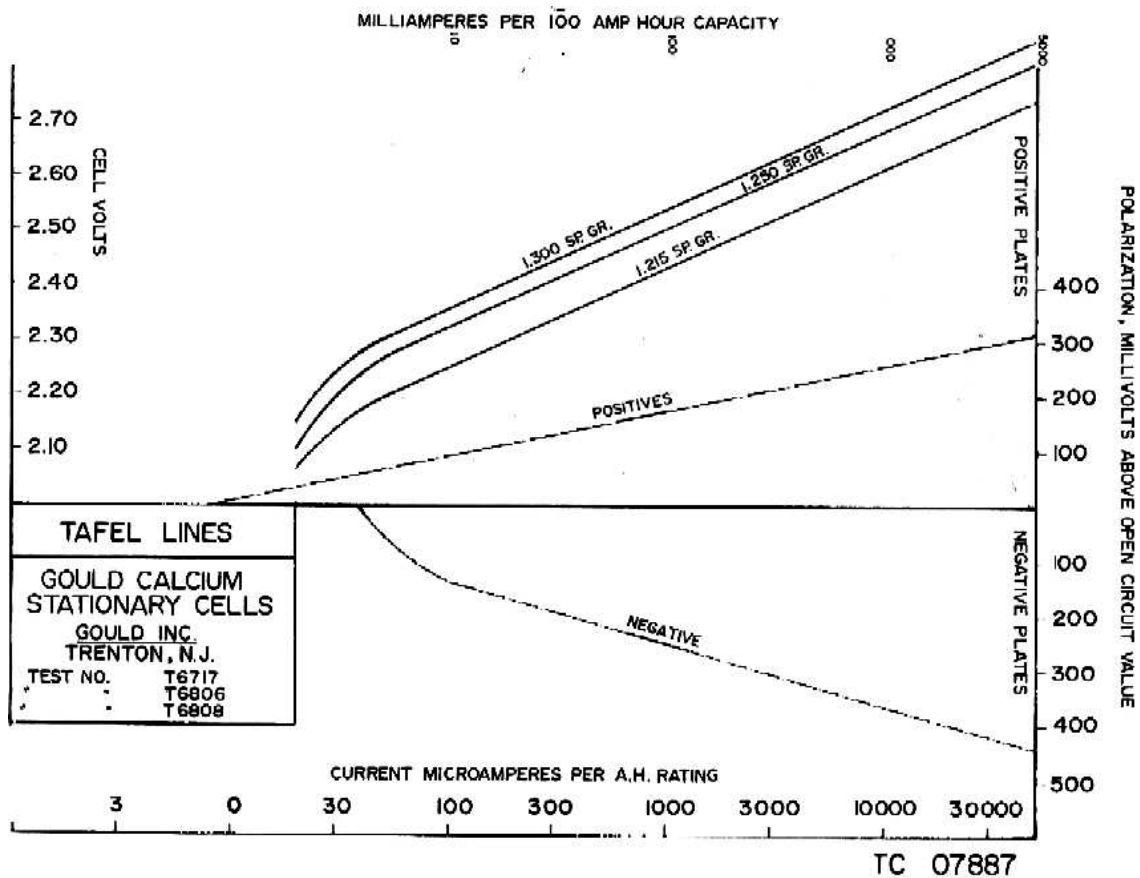


Figure 4, Tafel Curve Example

### Individual Cell Voltage Variation History

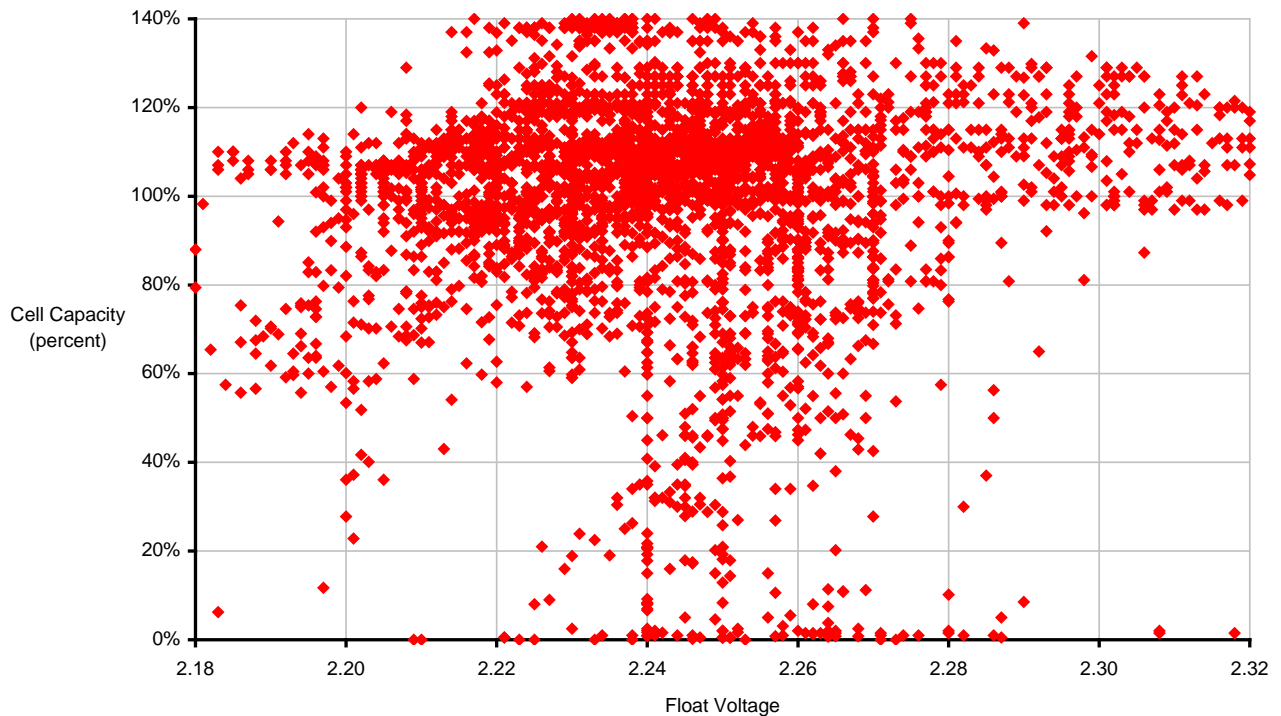
In addition to the technical issues that can be caused by ICV variation, there is also an historical concern. Lead-calcium cells were introduced in the 1950's. Until then and for many years thereafter, the principal technology was lead-antimony. The float current in lead-antimony cells is on the order of 10 times higher than lead-calcium. The higher float current and antimony transfer from the positive grid to the surface of the negative acting as a natural depolarizer, result in very tight ICV spreads. When lead-calcium was first introduced, users expected the same tight ICV spreads that they were used to lead-antimony.

This required manufacturers to develop other means to meet this expectation which probably accounts for the industry standard of +/-0.04vdc in most battery specifications. The most common is to produce the cells for a battery sequentially using the same material lots for the grids and paste. For vented cells, it is common (though not all do it) for the manufacturer to add a negative plate depolarizing agent to the cells to achieve more uniform float voltages. As the cells age, a natural balance begins to develop. At the same time, the depolarizing agent becomes trapped in the negative plates, such that at about 8 to 10 years of life, the agent is no longer a factor.

## Individual Cell Equalizers (ICE devices)

In its simplest form, an individual cell voltage equalizer (ICE) is a two-terminal voltage-controlled current shunt. The ICE unit is connected to the positive and negative terminals of each cell or multi-cell unit in a battery string. The ICE device provides each cell/unit with an alternate current path for string float current. The goal is to regulate the ICV of each cell within the parameters of the device. Specifically it is designed to reduce the voltage of high voltage cells. This causes the voltage across the low voltage cells to increase and in so doing ensuring that there are no weak cells in the battery.

Ensuring there are no weak cells in a battery string is a worthy goal. However, Electric Power Research Institute Inc. (EPRI), research<sup>5</sup> has shown that there is no correlation between ICV and cell capacity. While Figure 5 is specific to VRLA batteries (approx. 10,000 cells), the data for VLA batteries is similar with the exception that the minimum capacity observed was ~60% (approx. 25,000 cells).



**Figure 5, ICV Versus Cell Capacity**

The EPRI data along with our understanding of negative plate polarization variation calls into question the value of ICE devices. There is another potential issue. ICE devices are not capable of handling large currents. Therefore a short within the device would be burned open by the cell/unit it was connected across. The resulting open circuit would force the additional current required by the ICE devices through the cell/unit which would increase the positive plate grid corrosion and shorten the life of the cell/unit.

## So How Bad Can It Get?

For better or for worse, most of the time ICV variation is relatively stable over the life of the battery. Some cells may slowly creep up while some slowly slide down, but overall there is very little change. The data presented in figure 6 below, contradicts the normal experience. In contrast, it completely supports the EPRI research that shows there is no correlation between ICV and cell capacity. Two low voltage cells were removed from the battery and subjected to a full array of electrical tests and were then torn down and subjected to a full array of analytical tests. In terms of capacity, when the cells tested at over 100% capacity and all electrical tests were normal. In terms of the analytic tests, all parameters were within the manufacturer's specifications. The cells were produced sequentially using so far as possible the same batch lots for grids and paste.

The battery was installed in October 2001 and all cells were floating within the  $\pm 0.04\text{vdc}$  normal limits. At the first quarterly check after installation cells were found with ICVs of 2.14 to 2.15 while other cells were found with high voltages. An investigation with manufacturer support was started. In the interim it was decided to monitor ICV of all cells on a weekly basis.

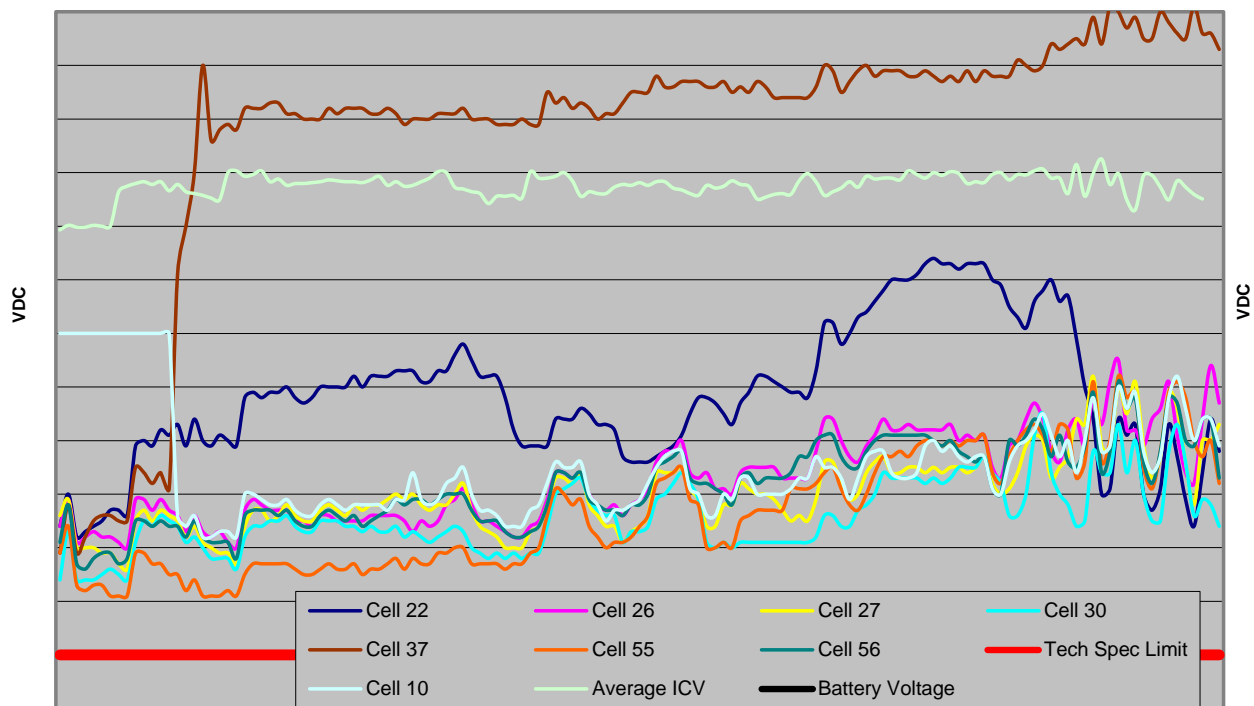


Figure 6, Sudden Rapid ICV Swings



## Conclusions

- ICV variation in lead-calcium batteries is a natural phenomenon that is not clearly understood and is normally not an issue with battery reliability or capacity.
- Reference electrodes provide useful data that allow the user to verify that ICV variation is not causing problems with a battery.
- Operation outside of the manufacturer's float voltage recommendations can result in shortened battery life and or cell failure.
- The minimum ICV for any cell is that required to maintain the cell in a fully charged condition.
- There is no maximum limit to ICV provided that the variation:
  - Is not caused by variation in positive plate polarization
  - The high voltage cells do not cause a low voltage cell to fall below the minimum voltage required to maintain it fully charged.
- Tafel curves provide the correlation between average ICV, plate polarization and float current and can be a useful tool in understanding battery performance.
- There is no correlation between ICV and cell capacity.
- The theory behind the use of ICE devices is not supported by our understanding of natural negative plate polarization differences and EPRI research on cell capacity verses ICV.

## References

1. Abstract from: "Individual cell voltage equalizers (ICE) for reliable battery performance," Lindemark, Bo ; Ericsson Components AB, Stockholm, Sweden, Telecommunications Energy Conference, 1991. INTELEC '91., 13th International, [http://ieeexplore.ieee.org/xpl/articleDetails.jsp?tp=&arnumber=172396&url=http%3A%2F%2Fieeexplore.ieee.org%2Fxppls%2Fabs\\_all.jsp%3Farnumber%3D172396](http://ieeexplore.ieee.org/xpl/articleDetails.jsp?tp=&arnumber=172396&url=http%3A%2F%2Fieeexplore.ieee.org%2Fxppls%2Fabs_all.jsp%3Farnumber%3D172396)
2. The Never Ending Pursuit Of Float Voltage Uniformity In Stationary Reserve Battery Plants David O. Feder; Electrochemical Energy Storage Systems, Inc. Gino Carosella; Stentor Resource Center, Montreal, PQ, Canada
3. The Effect Of Positive Polarization On Grid Growth, Cell Performance and Life "Willihnganz Revisited - 20 Years Later" W.B. Brecht, C&D Charter Power Systems, D.O. Feder, Electrochemical Energy Storage Systems, Inc., J.M. McAndrews, New York Telephone Company, A.J. Williamson, C&D Charter Power Systems
4. Storage Batteries, George Wood Vinal, Sc D. 4<sup>th</sup> Edition, John Wiley and Sons Inc., New York, 1955, Library of Congress Catalog Card Number 54-12826
5. Electric Power Research Institute Inc. Technical Report TR-1006522, "Stationary Battery Monitoring by Internal Ohmic Measurements"