Chapter Heading for
Encyclopedia of Electrochemical Power Sources

Henry A. Catherino
U.S. Army Research Development and Engineering Command
AMSRD-TAR-R/MS 121
Warren, MI 49397-5000
henry.catherino@us.army.mil

Abstract

The influence of ac on the operations within a cell is a very broad area of interest. In fact, dc responses can be considered as being a special case of an ac response where the cycle has a very long period. The approach taken in this present ion is to provide an overview by addressing the ac influence as a collection of special interest areas. This article shall address the following issues: RMS Heating, the application of a battery as a static filter for an alternator output, Electrochemical Impedance Spectroscopic (EIS) methodologies, pulsing of lead acid batteries during charge, and chaotic oscillatory behavior. This should give an indication of the scope of the ac influence.

Introduction:

The general topic of alternating current (AC) influence on the battery charging is necessarily a huge undertaking. The vast body of knowledge in electrochemical systems has been largely associated with direct current measurements. To place this into perspective, it helps to note that a direct current can be considered a special case of an alternating current where the frequency of the AC is zero (or, as a practical matter, has a frequency having a very long period).

In order to keep this presentation within reasonable limits, it will be presented as a collection of special interest topics that are connected with alternating current issues. Hopefully, this will give an indication of the breath and the scope of the AC influence.

RMS Heating:

An alternating current applied to an electrochemical cell contributes no net charge to that cell. From a Faradaic viewpoint, the second half of the cycle undoes what was accomplished during the first half of the cycle. Alternatively, from a resistive perspective, the Joule heating is independent of the direction of the passing current. In the case of an applied alternating current, it is helpful to estimate the effective value of that current that corresponds to an equivalent direct current producing the same heating effect. In short, the average power delivered to a resistor by a periodic current $i(t)$ is

Report Documentation Page

1. REPORT DATE **09 NOV 2007**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Basics: Cell Parameters AC influence on Charge Chapter Heading for Encyclopedia of Electrochemical Power Sources**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Henry A. Catherino**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Army RDECOM-TARDEC 6501 E 11 Mile Rd Warren, MI 48397-5000, USA**	8. PERFORMING ORGANIZATION REPORT NUMBER **18438**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **US Army RDECOM-TARDEC 6501 E 11 Mile Rd Warren, MI 48397-5000, USA**	10. SPONSOR/MONITOR'S ACRONYM(S) **TACOM/TARDEC**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **18438**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
Submitted for publication in "Encyclopedia of Electrochemical Power Sources", The original document contains color images.

14. ABSTRACT

The influence of ac on the operations within a cell is a very broad area of interest. In fact, dc responses can be considered as being a special case of an ac response where the cycle has a very long period. The approach taken in this present ion is to provide an overview by addressing the ac influence as a collection of special interest areas. This article shall address the following issues: RMS Heating, the application of a battery as a static filter for an alternator output, Electrochemical Impedance Spectroscopic (EIS) methodologies, pulsing of lead acid batteries during charge, and chaotic oscillatory behavior. This should give an indication of the scope of the ac influence.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**SAR**	**21**	

$$P = \frac{1}{T}\int_0^T i^2 R \, dT$$

where the period of $i(t)$ is T. The direct current power delivery is

$$P = i_{eff}^2 R$$

so the effective current affecting the Joule heating is

$$I_{eff} = \sqrt{\frac{1}{T}\int_0^T i^2 \, dT}$$

It should be noted that the square of the current is the essential term. The existence of a positive or negative current contributes equally to the net heat generated. Since the effective current is obtained by squaring the term $i(t)$, taking the average value of the squared function over the time period T and then taking the square root of the average of the squared function, the value of I_{eff} is the root-mean-square or rms current.

In the case of a sinusoidal wave form

$$I_{eff} = \frac{I_m}{\sqrt{2}}$$

where I_m is the maximum instantaneous current that characterizes the wave form. That is, I_m is the absolute value of the peak current delivered by the applied sinusoidal current.

This rms heating may or may not be a concern in any particular application. Since it does introduce a heating effect into an electrochemical cell, this necessitates an increase in temperature to dissipate that heat. The increased temperature influences mechanical and chemical processes taking place in the system. As examples, the thermal expansion of materials can affect the sealing effectiveness of a battery and the rates of chemical processes are an exponential function of the absolute temperature that serves to accelerate various failure modes.

Alternator Static-Filter:

Perhaps the best known application of ac charging in batteries is the use of these batteries as an automotive noise filter. The vehicle's alternator is placed in parallel with a battery

that is in turn connected to the vehicle's electrical load. This is most easily understood by examining the equivalent circuit diagram for a battery at higher frequencies. Figure 1 shows the dc polarization resistance as the sum of Rs and Rp. When a high frequency component appears across this network, the capacitor acts as a high pass filter that by-passes Rp. In effect, there is a lower resistance path through the battery. The battery provides a convenient ac path to ground across Rp. While this is going on, the battery is exposed to an ac component that is charging and discharging the battery. The net effect is that no net charging takes place but, the rms heating component exists. A discussion of the rms heating was presented earlier. The point is that the use of a battery as a high pass filter must be thoughtfully carried out.
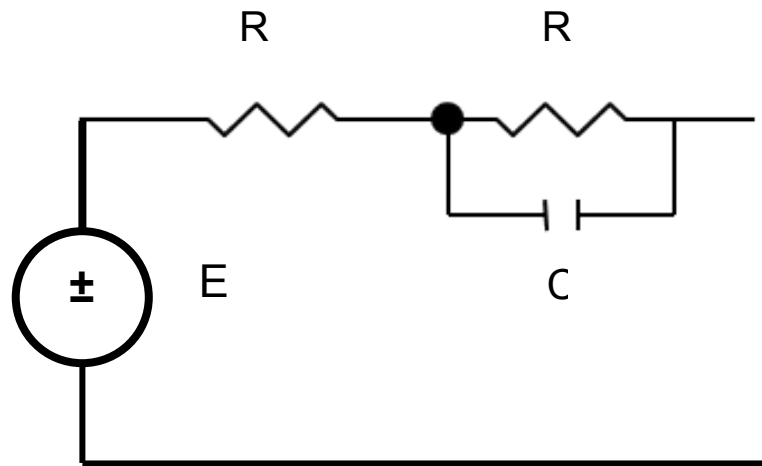

Figure 1. Equivalent circuit diagram of a battery power source showing components for approximating the battery behavior to include a higher frequency response.

EIS Methodologies:

Low level alternating current applications are areas of active study in the electrochemical discipline. The name given to the methodology is Electrochemical Impedance Spectroscopy (EIS). The objective here is not to review the depth and breadth of this technique but to provide an overview of the low intensity ac effect during charging. The EIS technique is a powerful technique in electrochemical research and a substantial body of literature stands behind it.

Essentially, the application of a low intensity ac signal to a battery provided a perturbation that barely disturbs the system. By doing that, the measurements that are made approximate those taken of a virtual equilibrium condition. The battery can be viewed as an electrical network and the ac signal is used to determine the impedance and phase angle of that network as a function of frequency. The techniques that have been developed for electrical network analysis can be applied to battery measurements. A

portion of an electrical network that approximately represents a battery is shown in Figure 1.

The circuit shown is that of a modified Thévenin power source and serves as an attempt to approximate a real battery over an extended frequency range. It is important to note that this is an approximation as the battery does exhibit (a) higher frequency inductive effects, (b) the positive and negative electrodes can exhibit distinct impedance responses, and (c) mass transport effects are not considered. This adds additional complexity to the model. In short, one can look at the application as an attempt to correlate the specific physical effects taking place within the battery to the linear circuit element components of an equivalent circuit.

There is an interesting point to be made here. Many of the presentations of the network that are presented in texts on electrochemistry tend to leave out the ideal voltage source and proceed with the analysis of the passive network. There is no real problem with that approach. A difficulty comes about when one tries to analyze the charging of a battery. The point is that the power absorbed by the battery during charging is the sum of the power dissipated across the equivalent series resistance in addition to the power absorbed or dissipated across the ideal voltage source. The point is that work is done on the system when one passes current through a voltage gradient. On the other hand, when the battery is discharging, the only power dissipated in the battery is that across the equivalent series resistance. The rest of the delivered power is dissipated (or stored) in an attached electrical load.

Practical applications of circuit analysis of this kind have been used in diagnostic tools for assessing the condition of the battery. The inverse of the impedance (i.e., the admittance) is a measure used in a well-known commercial device for assessing the condition of lead acid batteries. It is noteworthy that casual usage has referred to this methodology as a "conductance or conductivity" measurement. This approach minimizes the need for testing the battery under an applied load. Also, correlations have been made on the values of the circuit components as a measure of state of charge and state of health of a battery system. Applications such as these are useful in the development of smart batteries and battery management systems.

AC Effects during Over-Charge:

For the discussion that follows, the growth of resistance shall be postulated as the consequence of electrolyte being displaced out of the inter-electrode gap by gas generation as it occurs in sealed cells. The gas could be the oxygen that is generated by the overcharge reaction taking place as part of the closed oxygen cycle. It is noteworthy that this hypothesis builds upon many of the fundamental concepts identified previously by Pavlov.[1]

Actually, the proposed hypothesis is not very original. Other workers have observed this behavior in clear plastic cells. Test VRLA cells show an electrolyte rise in the cells when the cells begin to gas. This is an obvious displacement of the electrolyte by the gas

produced. Starved cells such as the starved electrolyte Nickel Cadmium wound roll have been observed to fizz and drip electrolyte when placed into overcharge. By replacing the highly conductive electrolyte with nonconducting gas would lead one to conclude that the resistance within the inter-cell gap is increasing. This whole mechanism was almost fully described by Weighall as he discussed the influence of capillary pressures on preferential cell filling by the electrolyte.[2]

The object of the study that follows was to measure the impedance and phase angle as a function of frequency as a VRLA battery goes into overcharge. The experimental approach was to fully charge the battery and then bleed off some of the charge. The battery was then put back on charge and repetitive EIS sweeps were taken as the battery went into overcharge. The charger was limited to 3 amperes and the voltage limit was set at 15.5 volts. The data was resolved to fit the equivalent circuit shown in Figure 3.

Table 1. Resolved values of Rs, C and Rp fit the equivalent circuit shown in Figure 3.

run	Rs	C	Rp
1	0.00287	10.48	0.00363
2	0.00286	7.38	0.0061
3	0.00281	5.709	0.01577
4	0.00285	5.225	0.03119
5	0.00292	4.725	0.12134
6	0.00287	4.504	0.12702
7	0.00286	4.353	0.10791
8	0.00283	4.313	0.2202
9	0.0029	4.313	0.6323
10	0.00288	4.33	0.77724
11	0.00286	4.323	0.79293
12	0.00289	4.282	0.74458
13	0.00285	4.273	0.8281
14	0.00286	4.261	0.82805
15	0.00293	4.242	0.82254

For the sake of clarity, the charger used was a standard float charger designed for charging automotive batteries. The calculated equivalent series resistance of the charger is 5.2 Ohms. The naturally occurring parasitic current passing through the battery also passes through the equivalent series resistance. The open circuit voltage of the charger minus the IR drop across the equivalent series resistance is the voltage applied to the battery. The consequence of all this is that the charging voltage falls within the established range for an automotive lead acid battery charging. The test conditions are not abusive and no cell venting occurs.

The specific values obtained during each of the scans are given in Table 1. The scans were successively taken. The scan identified as run 1 was taken with no applied charge current as a reference point. The subsequent runs had the charger attached.
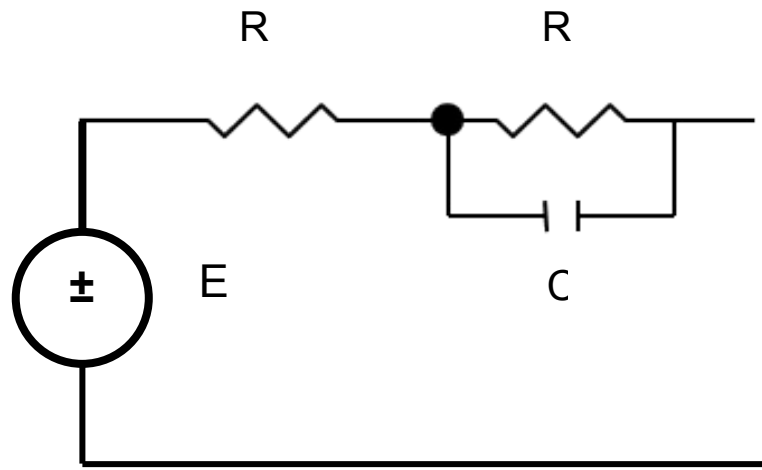

Figure 3. Repeat of Figure 1 showing the equivalent circuit diagram that was fit to the data obtained by the EIS technique

The values obtained are illuminating. The values of Rs basically remained constant. Rs represents the resistance associated with the kinetics of electron transfer. Rp represents the resistance associated with the ionic charge transfer through the solution. Finally, C represents the interfacial capacitance associated with the electrochemical cell.[3] The values of Rs hardly changes as the battery goes into overcharge. Alternatively, Rp shows a huge change in excess of two orders of magnitude. This large change in resistance is what was anticipated from the postulated hypothesis and found.

There is another interesting feature about this data and it becomes evident when the data is plotted as shown in Figure 4.

Figure 4 shows the capacitance decreases first. As the capacitance decrease stabilizes, the resistance makes its move to higher values. What is interesting about this data is that it is

perfectly consistent with the new hypothesis. That is, the gas generation model that displaces the electrolyte can explain this behavior.

To show that this behavior is consistent with the postulated hypothesis, it is necessary to review some fundamental physical concepts. Capacitance is defined as:

$$C = \varepsilon_0 \, A^*/d$$

where C is the capacitance, ε_0 is the dielectric constant, d is the separation of the plates of the capacitor and A^* is the plate area. In the case of resistance:

$$R = \rho \, l/A$$

where R is the resistance, ρ is the resistivity, l is the length of the resistive path and A is the cross-sectional area of the resistor.
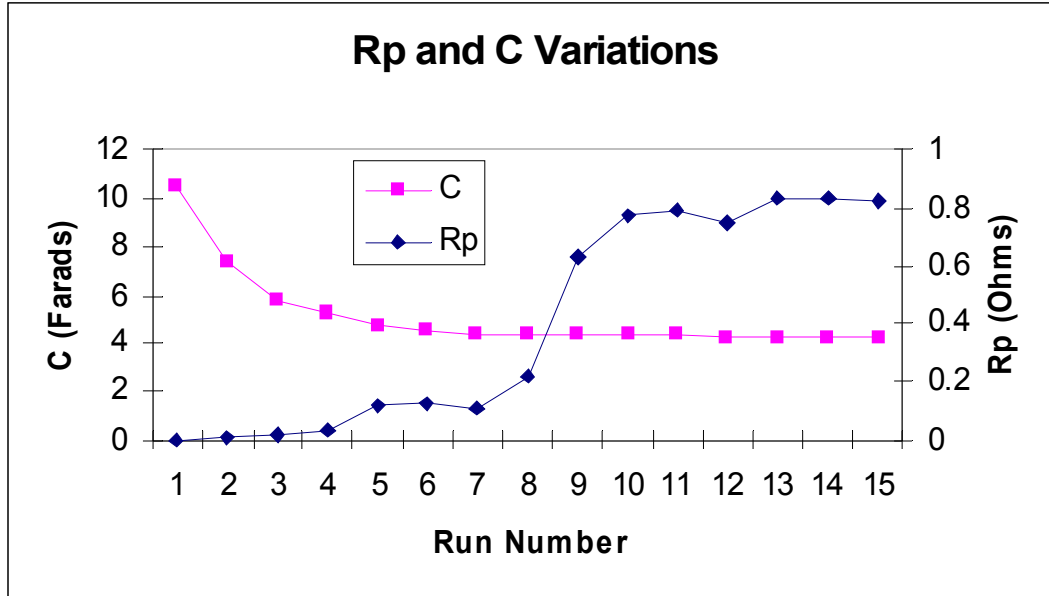

Figure 4. Comparison of the capacitance the resistance changes in the order of their measurement.

Two key observations need to be made here. The first is that A^* and A are not the same. A^* represents the interfacial surface area where charge can be stored by some sort of charge separation. A, on the other hand is the cross-sectional area of the resistor. It represents the projected area of the surface as if it were planar. The inner surfaces of a porous electrode that do not face the counter electrode do not participate in determining the area term. Clearly,

$$A^* \neq A$$

In fact,

$$A^* \gg A$$

The next observation is that the dielectric constant for a conductive ionic aqueous solution is about 30 and that of a gas such as oxygen is approximately 1.00. Also, the resistivity of an aqueous ionic solution is very low compared to a gas, which is virtually infinite.

With these considerations in mind, we can visualize a hypothetical pore in a flat surface as that shown in Figure 5. Certain liberties were intentionally taken in illustrating the pore in this way for the sake of conceptual convenience. However, the analysis would apply to all pore geometries. At this point, the rationalization that is consistent with the EIS data becomes evident. Taking the new hypothesis as being operative, gas generation begins over the entire surface. The gas bubbles on the front surface have no barrier and can move away from the surface. However, the gas bubbles generated within the porous matrix are basically trapped.
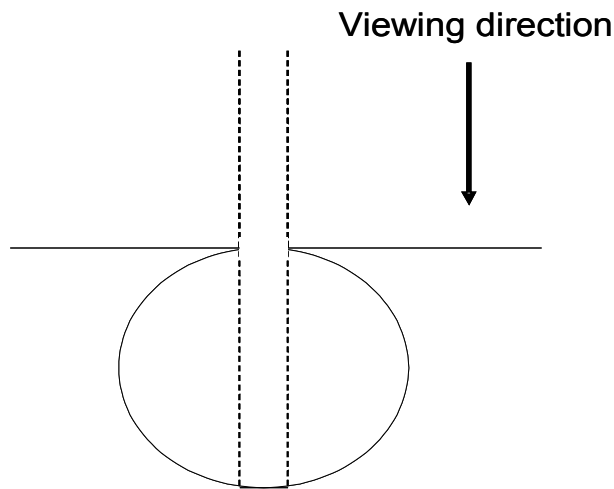
Simulated Pore

Figure 5. Idealized comparison of actual vs. projected surface of a pore.

The argument follows directly. As a gas bubble fills the pore and covers the wall surface of the pore, the area that affects capacitance is covered by a medium having a lower dielectric constant. However, the area that controls resistance is very small (as shown by the dashed lines on the lower pore surface). The resistance change caused by the gas bubble within the pore is a small effect relative to the capacitive effect. It is of interest that this observation should be made in all cases where a gas is evolved within a porous matrix.

Another interesting point can be inferred from the preceding discussion. It is to be noted that the interfacial capacitance decreased by about one-half. Since the interfaces have, in this case, a total applied voltage of about 14 volts, the capacitor, as shown in the circuit diagram, is charged and must discharge about half of its stored energy as a direct consequence of the change in interfacial capacitance. This energy is converted to heat by discharging across the resistor Rp shown in Figure 3. This is a relatively small quantity when considering the size of the battery but this released energy is converted to heat at the immediate electrode interface.

Pulsing of Lead Acid Systems:

The discussion here relates to current pulsing. As a point of clarification, one can always do a Fourier analysis on any periodic wave form and fully describe that wave form as a summation of pure ac sinusoids having different frequencies. In this context, pulse effects applied to a load can also be viewed as an ac response to that same load.

The effect of applying current pulses to flooded lead acid batteries has revealed some interesting effects and has found some practical applications. The application of current pulses to the cell formation for lead acid cells has been shown to decrease the formation time. This is already a commercial practice. Also, the Australian Navy has adopted this pulsation technique as a means for restoring the performance of its submarine batteries. [4] The pulsation equipment design was derived from the methodology detailed by Lam et al. [5,6] In those studies, the photomicrographs showed that the effect of the pulsations resulted in changes in the lead sulfate crystal morphology.

This effect is relatable to the fact that the electrolyte is a reactant in the chemical reaction that is the energy storage mechanism. The effect is also connected to the cell design that allows a relatively free movement of electrolyte. The AGM and GEL versions of the VRLA design minimize the effect by providing a means for constraining convective electrolyte movement. Although the interpretation of the effect is far from complete it is notable that during the charging process of a lead acid battery, concentrated sulfuric acid is produced at both electrodes. Since the specific gravity of concentrated sulfuric acid is about 1.8 and the normal electrolyte specific gravity is about 1.2, the natural process is for the sulfuric acid that is produced during charging at both electrodes to sink to the bottom of the cell. If the electrolyte movement is not constrained, as is the case in flooded battery designs, the consequence of this is the electrolyte stratification effect. This effect is well known and often observed during the deep cycling of flooded lead acid batteries. Also, there is a natural convective stirring taking place in the vicinity of the electrodes.[7] It was argued in this reference paper that two distinct regions occur during the constant voltage charging of a flooded lead acid battery. The analysis was performed as a simulation based on reasonable assumed physical models.
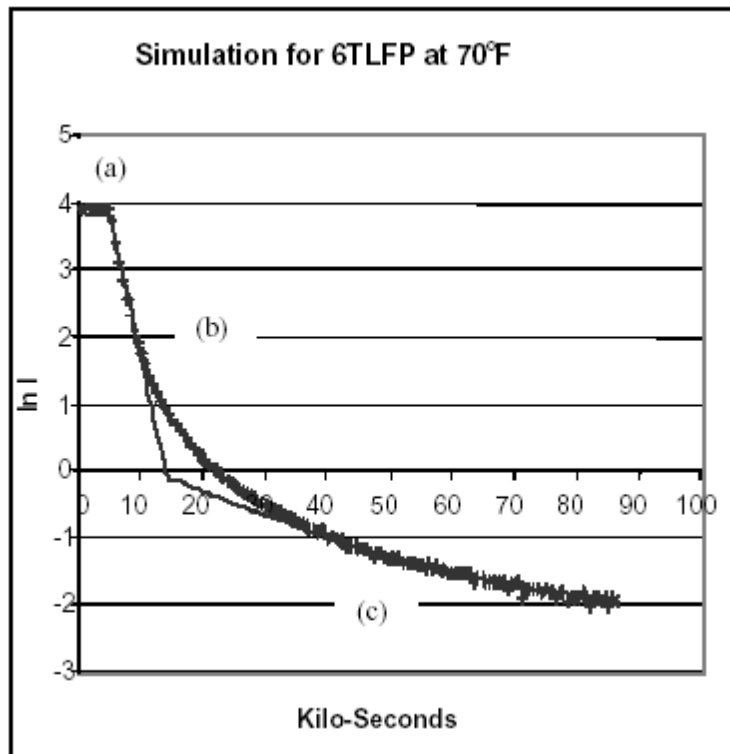
Figure 5. Comparison of measurements from Constant Voltage model and steady state measurements.

The regions of interest in the overlaid simulation (starting at the extreme left) are:

(a) the flat constant current segment representing the current limit of the power supply used to make the measurements;

(b) that segment where the concentrated sulfuric acid flows out of the pores of the electrode and flows downward along the electrode interface as the consequence of its greater density relative to the bulk electrolyte. Under normal charging conditions, the applied voltage for the six cell battery is about 14.2 volts and at this polarization, the concentration of sulfuric acid can achieve its maximum value, i.e., that of concentrated sulfuric acid (~18M).

(c) the third segment represents the region where a diffusional mass transport through a boundary layer is sufficient to provide a convective mass transfer of the sulfuric acid away from the interface without the dependence on density gradients. This latter segment shows a curvature which is caused by the superimposed effect of the steady state self-discharge current. Upon correcting for the self-discharge current component, the segment becomes linear.

The downward flow of sulfuric acid does not permit the creation of a well-formed boundary layer in segment (b). The reason is that the sulfuric acid flow is first normal to the surface as it exits the porous electrode matrix and then cascades downward. The deviation would then be the transition to a stabilized boundary layer required in segment

(c). The dynamics of the stabilization is not considered in the model. The model assumes that the transition is instantaneous.

An interesting inference can be made here. If the density gradients are producing a stirring action, can this stirring effect be enhanced? This appears to be the case. By controlling the magnitude of an applied charging pulse and controlling its repetition rate, one can affect the rate of stirring and as a consequence, the mass transport conditions at the electrode interface. This is interpreted as a reduction in the boundary layer thickness which controls the rate of mass transfer. Also, a forced convection of this kind can affect the pH gradients within the electrode active mass.

To interpret this effect, the observed current enhancement can be modeled by observing that the mass transfer under convective mass transfer is given by:

$$i = nFAD\left(\frac{C - C_0}{\delta}\right)$$

where δ is the boundary layer thickness. All of the other parameters are either geometric or physical constants, (i.e., n is the number of equivalents per mole, F is the Faraday, A is the projected electrode area, D is the diffusion coefficient and $C-C_0$ is the linear concentration gradient). The efficiency of interfacial stirring serves to diminish the boundary layer thickness resulting in an observed current enhancement.

It would seem reasonable that stirring could be induced by the application of charging pulses to the electrodes found in flooded lead acid batteries. This could be accomplished by taking advantage of the existence of the density variations at the interface. The following study illustrated this effect.

Basically, the objective of the study was to observe the effect of pulsation on the rate of mass transfer to small test electrodes. For these studies, plates of dimensions 20 x 10 x 2.5 mm were formed. The paste was prepared by mixing a typical Barton pot with lead oxide, sulfuric acid and water. Barton pot leady oxide contained 21% free lead. Free lead was a core of each fine lead oxide spherical-shaped particle.

A typical cell used in these studies consisted of one positive plate (PbO2/PbSO4 electrode), two negative electrodes, and two separators in between. A noble metal (platinum mesh) was used as a negative electrode.

A microporous polyethylene separator with pore size 0.03 μm, thickness 0.3 mm, porosity 60% and electrical resistivity 1.86 mOhm/cm^2 was used to separate platinum mesh from the positive plate. An assembly of a Pt electrode, a positive electrode and the separator was placed in a specially designed Teflon electrolytic/galvanic container filled with sulfuric acid solution (d = 1.25 g/cm^3). The plates were allowed to stand in the sulfuric acid solution for 60 min at 25°C. A DC current 0.5 A was used to form the plates. The formation process took about 5 hrs. After formation each cell was kept at open circuit for one hour at 25°C. The Teflon container with the cells was placed in a

water bath maintained at 25°C. The measurements were performed by using a three-electrode system consisting of a PbO_2 (positive electrode), a platinum mesh counter (negative electrode) and a cadmium rod (reference electrode). A current flow was measured between the PbO_2 and platinum electrodes while the potential was measured between the PbO_2 and cadmium electrodes. In these studies, a broad range of current densities was used in a charging/discharging process including high-density current not normally used in commercial lead acid batteries (due to overheating).

In this set of experiments, a constant voltage was applied to the cell and the resulting limiting current was measured. Next an applied square wave pulse train was superimposed on the applied voltage and the resulting limiting current was measured. Figure 6 shows the effect of the superposition. The consequence of the application of the pulses is shown in Figure 7. The effect is clear that the application of the pulses enhanced the limiting current well in excess of that corresponding to the smallest value of voltage summation (i.e., the bottom of the square wave). Figure 7 also defines the parameter, Δi, which is the change in the average limiting currents. This parameter is a function of waveform, amplitude and frequency. By monitoring this parameter, an examination of the sensitivity of the pulsed waveform on the induced stirring became possible.
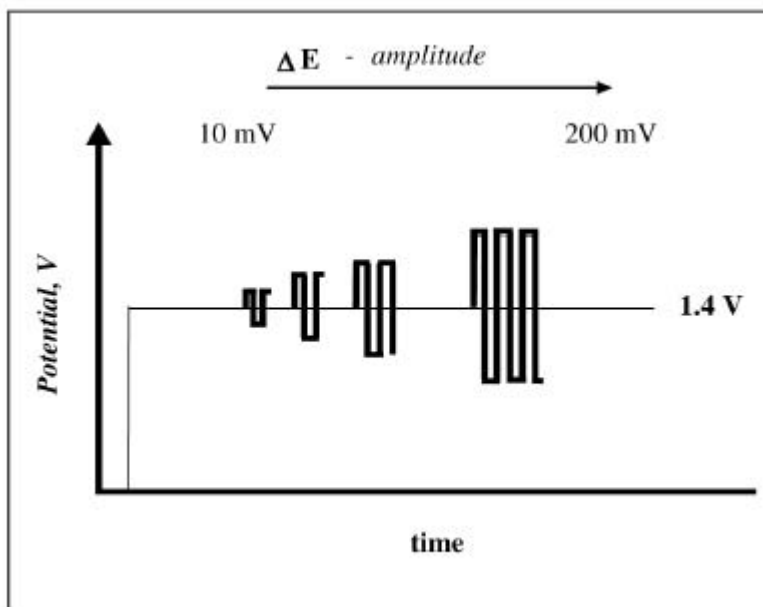

Figure 6. An alternating square wave of varying amplitude superimposed on constant potential (1.40 V)
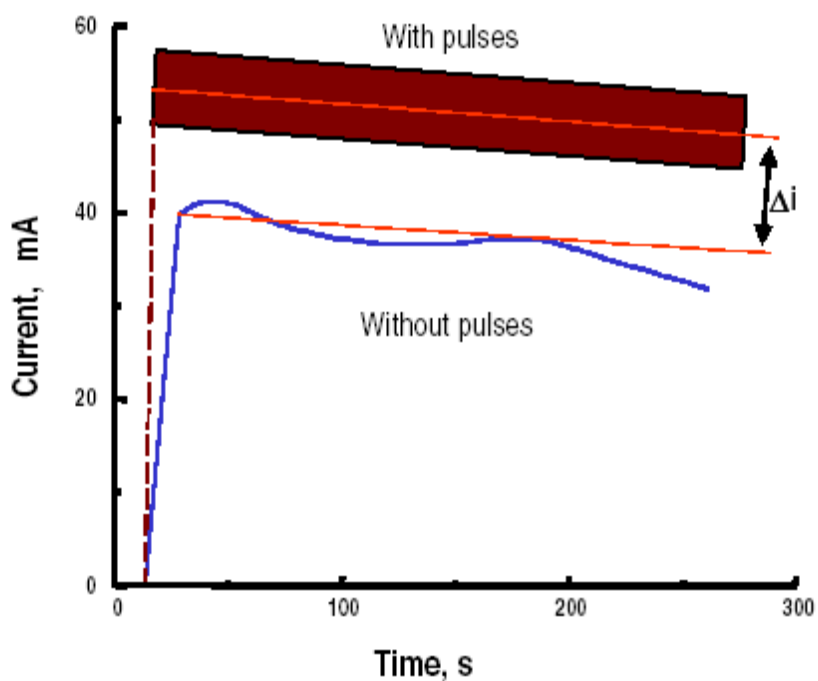
Figure 7. Amperometric curves (constant potential 1.40 V) showing a charging current into the positive electrode with pulses and without pulses (amplitude 100 mV, frequency 200 Hz)

As a consequence, one can expect changes in the crystallographic and morphological structure of the active mass of the electrode materials. The stirring reduces pH gradients within the pore structure and the pH should affect the morphology of the resulting crystalline mass. This appears to be the case. [8] The application of periodic current pulses during charging, provided that the pulses are of sufficient intensity and are repeated at some optimal frequency, does show beneficial effects on electrodes of a lead acid chemistry as a consequence of induced stirring.

Chaotic Oscillations:

An interesting event that is occasionally reported is the oscillatory behavior of VRLA batteries when they go into overcharge. In this case, the oscillatory behavior is the response to the application of constant voltage to the battery. Figure 8 shows a military grade VRLA 12 Volt – 120 Ah battery showing this behavior. The battery was pretreated to induce the effect and the pretreated battery was then charged at a normal 14.25 Volts with the consequent result.
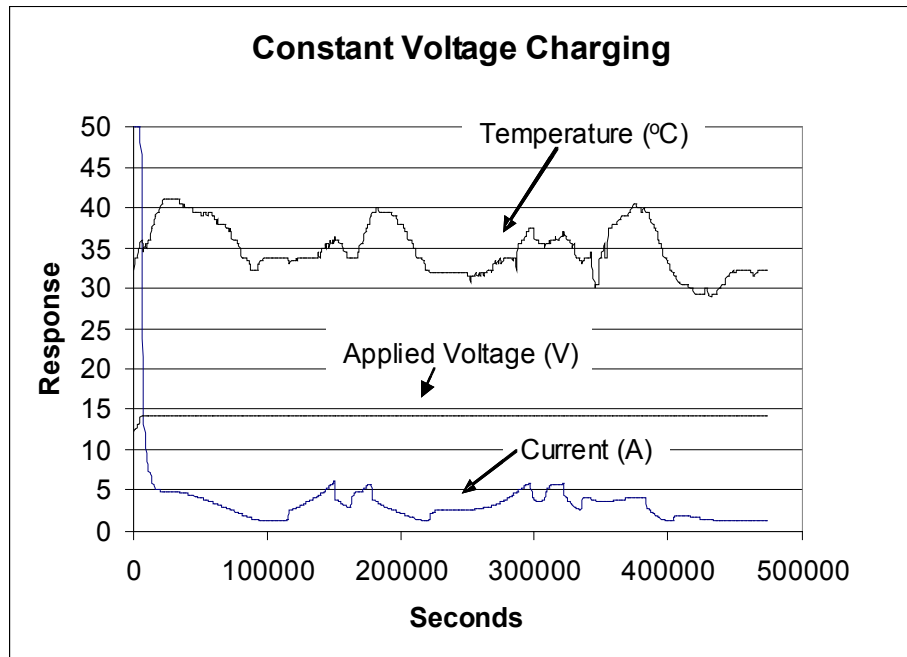
Constant Voltage Charging

Figure 8. Charging profile of a 12V – 120Ah military grade VRLA battery.

Rather than revealing the expected fall off of current that normally takes place during charging, the current exhibits a chaotic oscillatory behavior. The interpretation given to this effect is interesting as it emphasizes the point that a battery is a complex system. The interpretation given is that two competing processes are taking place. As the battery is gassing, electrolyte is displaced from the intercell gap. This raises the internal resistance. The increased IR drop acts to reduce the voltage that is driving the gas evolution reaction (because the battery is being charged at constant voltage). At the same time, the heat generation raises the temperature of the battery so as to enhance the rate of the gas evolution reaction. There are two competing processes driving the net process in different directions. One is trying to generate a thermal runaway and the other is attempting to stabilize the process to achieve the normally expected behavior. What makes this interesting is that the competing processes are non-linear in their behavior. That is, both processes are exponential functions and, as such, a non-linear behavior is expected. Depending on the coupling between the development of the cell's IR drop and the system temperature (i.e., I^2R heating), three states appear as possible solutions. Two were described above, i.e., stabilization and thermal runaway. The third state is an oscillatory condition taking place between the exponential processes. Strictly speaking this is insufficient to define a chaotic state. However, the battery contains 6 cells in series and the cells are not necessarily identical in performance. This additional dimension of the competing cells in series can generate the observed chaotic behavior.

The implication of this observational point is the identification of complexity as an aspect of the battery system. This suggests that complexity theory should find a home in the study of battery behavior.

It would be instructive to further clarify the concept of complexity as applied to battery systems. To enter this discussion, it is necessary to review the issues of linearity and non-linearity in the modeling of physical systems.

The basic description of a linear system is that it conforms to the following restrictions: [9]

$$f(a + b) = f(a) + f(b)$$
$$cf(b) = f(cb)$$

Although both equations define the concept, a brief discussion of the first equation is of interest here. Basically, the first equation says that if one fully understands the response of component (a) and component (b), then the response of the summation of components (a + b) are determined. There are many examples of this cited in textbooks and formal courses of study. In fact, one finds them in science, engineering, management, etc. One classic example and application is the Principle of Superposition.[10] Unfortunately, the world of experience tends to quickly reveal deviations from linear behavior.

A simple way of addressing non-linearity is to acknowledge the deviation from linearity.

$$\delta + f(a + b) = f(a) + f(b)$$

Here, δ is shown as the deviation from linear behavior. Analytical solutions to non-linear problems are not as clear cut as the mathematics developed for analysis of linear systems. But such tools exist. It is not the purpose here to develop an exposition of the available analytical methods, but to give a simple but practical approach. Discrete dynamical approaches can be used that resemble the method of successive approximations.[11]

$$\delta + f(a_{n+1} + b_{n+1}) = f(a_n) + f(b_n)$$

What this expression is attempting to convey is that by first making an estimate on one side of the equation the other side can be corrected in an attempt to minimize the deviation from linearity. The iteration then continues with the hope that an "equilibrium" point is found where:

$$a_{n+1} = a_n$$
$$b_{n+1} = b_n$$

In short, solutions are not always unique if they exist at all. The result of this effort yields results such as convergence, divergence, a limit cycle or chaotic behavior. These observations fall into a grouping known as complex behavior. This is an area of substantial interest in the mathematical and the scientific communities.

A complex system can be characterized by unique behaviors such as:[12]

Self-organizing behavior
Sensitive dependence on initial conditions
Chaos

What follows is a demonstration that a battery shows the properties of a complex system. If this is the case, the notion of arriving at a complete battery model must take a different direction than the usual application of linear modeling techniques.

Self-organizing Behavior. Observations of the charging of a flooded lead acid battery have long revealed the general behavior shown in Figure 9. [13]
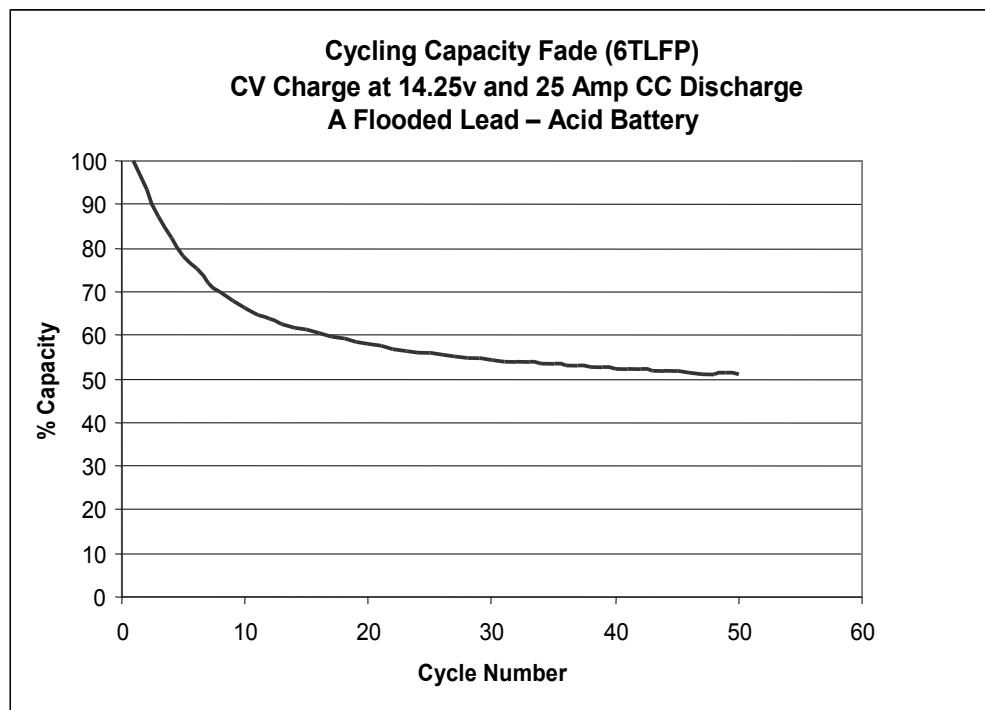

Figure 9. Successive cycle behavior of a flooded lead acid battery.

This figure shows the observed loss of capacity that is attributed to the phenomenon known as electrolyte stratification. In short, as the battery is charged, concentrated sulfuric acid is produced at the electrodes. The concentrated acid has a density of 1.8 as compared to that of the electrolyte which is about 1.2. The high density acid settles to the bottom of the cell and collects there. The loss of capacity is the consequence of the sulfuric acid being selectively removed from the top of the cell and accommodated at the bottom of the cell. Since sulfuric acid is one of the reactants in a lead acid battery, the top of the cell is starved of one of the reactants that is in overabundance at the bottom of the cell. Figure 10 shows the effect of stirring the electrolyte by overcharging the battery

so as to mix the electrolyte and restore the sulfuric acid distribution in the cells of the battery.

The gassing within the cells during overcharge restores the capacity of the battery by mixing the electrolyte. The sequence is repeated to demonstrate the reproducibility of the effect. It is noteworthy that the batteries having antimonial grids eventually provide sufficient internal gassing to mix the electrolyte and in so doing, maintain a higher capacity during repetitive cycling.

Ampere Hours Delivered on 25A CC Discharge to 10.5 Volts Vs Cycle
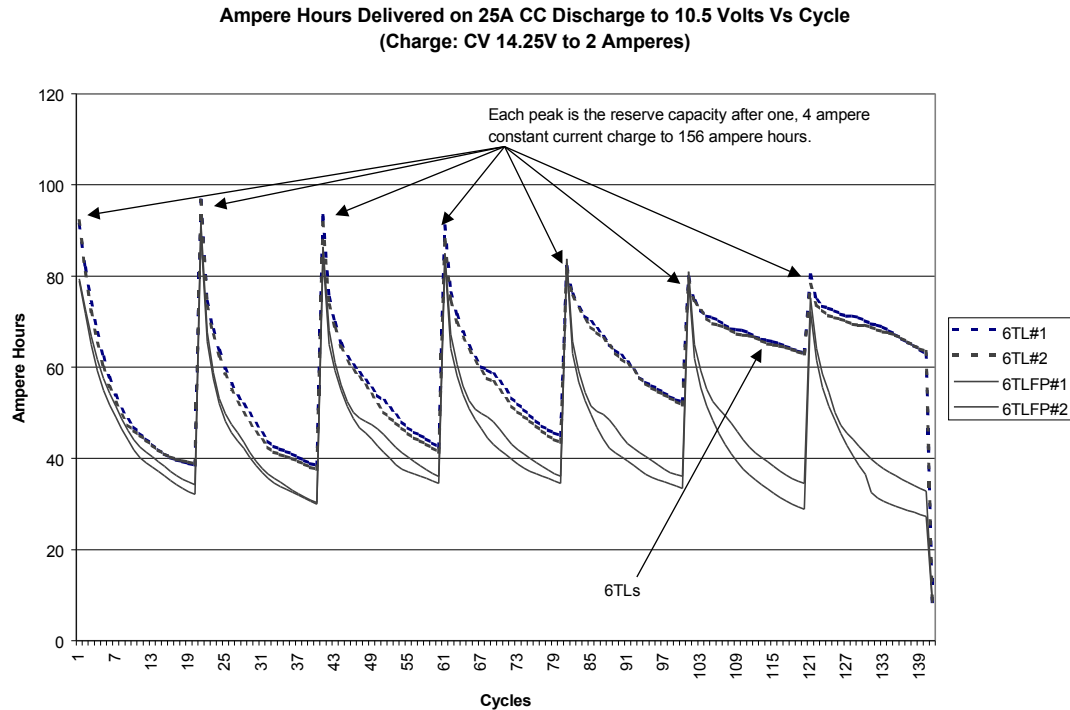**(Charge: CV 14.25V to 2 Amperes)**

Figure 10. Effect of gassing on overcharge during the repetitive cycling of batteries. The 6TL design has an antimonial alloy positive grid. The 6TLFP has a calcium alloy positive grid.

The point behind raising this stratification effect is that during the cycling of a battery a concentration gradient is developed that is stabilized by gravity. Unassisted, the mixing takes place by a diffusive mass transfer which is a very slow process. The existence of the concentration gradient is a non-equilibrium condition. In effect, as a lead acid battery is cycled, a concentration gradient appears which did not exist previously. This concentration gradient constitutes an ordering of the system. With respect to the electrolyte, a decrease in Entropy has taken place. This is evidence for self-organizing behavior.

Sensitive Dependence on Initial Conditions. There was a time when the failure of lead acid batteries was characterized as due to a generic cause known as Sulfation.[13] This is actually an example of an attempt to impose linear behavior on lead acid battery

degradation. In fact, Sulfation used in this way represents the name given to the set of all failure modes that a lead acid battery can experience. Continued technological development allowed the failure modes to be better identified and understood mechanistically (to a greater or lesser degree). A listing of the major failure modes is presented in Table 2.

There is an observation that needs to be made here to bring the notion of a failure mode within the confines of complexity theory. It is to be noted that the rate of change of any performance variable with respect to time goes to zero when a battery failure takes place. This means that these failure modes can be considered as having the property of being equilibrium points. In complexity theory, these failure modes could be identified as "fixed point attractors."

Table 2. Listing of the lead acid battery failure modes

<div align="center">Major Lead Acid Battery Failure Modes</div>

- Loss of electrolyte
- Electrolyte stratification
- Hydration
- Grid corrosion followed by detachment
- Internal shorting
- Lead oxide film formation at positive current collectors
- Agglomeration of finely divided lead at negative electrodes
- Electrolyte contamination
- External damage to case and terminals
- Hard Sulfation
- Inter-cell connector failure
- VRLA unique failure modes
    - Thermal runaway
    - Lead sulfate accumulation at the negatives

It is very difficult (if not impossible) to predict the failure mode of a new battery before it is placed in service. However, the manner of use or of testing could affect the number of likely failure modes that could influence the eventual failure. Those failure modes that might bring about the failure constitute the "domain of attraction." How the battery fails depends upon how it is used (and how it is built). This illustrates the effect known as sensitive dependence on initial conditions.

Chaotic Oscillations. An interesting situation occurs occasionally when one attempts to induce a VRLA battery into thermal runaway.[14] A transition zone between stable operation and thermal runaway exists wherein the battery enters into electrical oscillation. The effect is an interesting one. This effect is the consequence of a competition between two exponentially controlled processes. The rising temperature exponentially accelerates the oxygen evolution reaction (i.e., the Arrhenius Equation). However, the oxygen evolution process displaces the electrolyte in the inter-electrode gap. This process creates an increasing cell IR drop. When under an applied constant cell voltage, the increased IR

drop suppresses the driving voltage of the electrode reaction which is also an exponential function (i.e., the exponential form of the Tafel Equation).   The two nonlinear processes involve an accelerating effect and a retarding effect. Also, since there are 6 cells in series in this battery, the interaction between the cells gives rise to this chaotic behavior. See Figure 11 for a visualization of the effect.
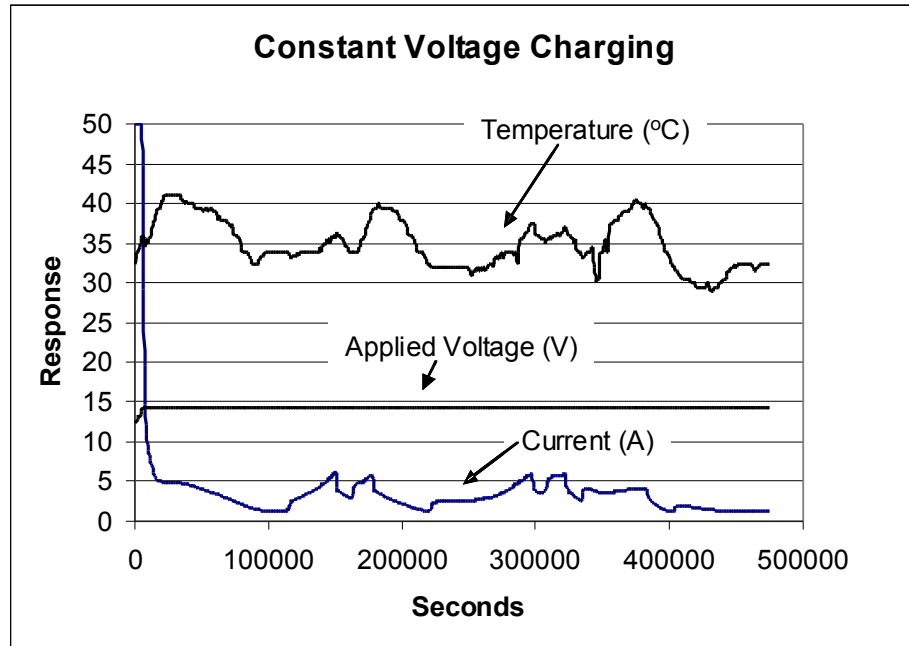

Figure 11. 120 Ah 12 V military grade AGM battery in oscillation during overcharge at an applied 14.25V. The temperature was measured at the negative terminal.

This represents a demonstration of chaotic behavior in a battery which is a defining characteristic of a complex system.

Observation:

The AC response of electrochemical cells makes a compelling argument for demonstrating the complexity of electrochemical systems. This observation infers that studying the individual parts of the cell with the hope of summing the knowledge thus obtained as means for fully describing the electrochemical cell behavior is not achievable. The preceding statement is nothing more than observing that the physical and chemical response models operative within an electrochemical cell are nonlinear. The hope for seeking a complete description of the cell by the summation of individual effects presumes that the system is composed of linear models. That is, the presumption is made that the principle of superposition is applicable. This appears not to be the case. The nonlinear interactions give the cell properties similar to a biological system by virtue of the display of complex behavior. The behavior of an electrochemical cell requires an

approach that acknowledges its complexity and, as a consequence, this opens a fertile area for research into complex systems.

References:

1. Pavlov, D., "Energy balance of the closed oxygen cycle and processes causing thermal runaway in valve-regulated lead/acid batteries," J. Power Sources 64 (1997) 131-137.

2. M.J. Weighall, "Function of Separator in the VRLA Battery," in: Valve Regulated Lead Acid Batteries, Elsevier, 2004, D.A.J. Rand, P.T. Moseley, J. Garche, C.D. Parker, Editors, p. 169.

3. A.J. Bard and L.R. Faulkner, "Electrochemical Methods," John Wiley and Sons, 1980, pp. 316-353.

4. Melvyn James, Jock Grummett, Martin Rowan and Jeremy Newman, "Application of pulse charging techniques to submarine lead-acid batteries," Journal of Power Sources, Volume 162, Issue 2, (22 November 2006), pp 878-883.

5. L.T. Lam et al, Journal of Power Sources, 53 (1995) 215-28.

6. L.T. Lam et al, "Pulse-Current Charging Techniques for Lead/Acid Electric-Vehicle Batteries," Advanced Lead Acid Battery Consortium, ILZRO, Report Number DMR-536, April 1997.

7. H.A. Catherino, P. Shi, A. Rusek and F. Feres, SAE Technical Paper Series, Society of Automotive Engineers, Paper 2000-01-0305.

8. D. Pavlov, "Influence of H2SO4 concentration on the mechanism of the processes and electrochemical activity of Pb/PbO2/PbSO4 electrode," Journal of Power Sources, 17 (2004) p. 288.

9. Buck, R.C., Advanced Calculus, McGraw-Hill, Third Edition, 1978, p.334.

10. Hayt, W.H., and J.E. Kimmerly, Engineering Circuit Analysis, Fourth Edition, McGraw-Hill, 1986, p.74.

11. Sanderfur, J.T., Discrete Dynamical Modeling, Oxford University Press, New York, 1993.

12. Nicolis, G. and I. Prigogine, Exploring Complexity, W.H. Freeman and Co., New York, 1998, pp. 5-44.

13. Catherino, H.A., F. Feres and F. Trinidad, "Sulfation in Lead Acid Batteries," J. Power Sources, Volume 129, Issue 1, 15 April 2004. pp. 113-120.

14. Catherino, H.A., "Complexity in battery systems: Thermal Runaway in VRLA batteries," J. Power Sources, Volume 158, Issue 2, 25 August 2006, Pages 977-986.