Detecting Incipient Deterioration in Standby Batteries

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Note: The term 'cell' is used here to indicate a cell, jar (US) or monobloc of any voltage

Introduction

Over the last 40 years, the standby battery industry has become dominated by the Valve Regulated Lead-Acid (VRLA) battery. These cells are used to support AC and DC Uninterruptible Power Supplies (UPS) and key applications in many areas of safety, finance and data, and must supply power upon mains failure with no discernible break in the supply waveform. These batteries are held on a very low float charge continuously to maintain capacity and it is not unusual for the cells to be prone to various failure modes, including accelerated plate corrosion, early sulphation and electrolyte 'dry-out', the latter predominantly in the USA. In capacity tests of more than 24,000 cells, from the US, UK and Pacific Rim countries, over 60% failed well before their intended design life [1].

Example of a 1048-cell standby battery

Since all standby batteries are connected in series or series-parallel to obtain the voltage and power necessary for the application, the failure of a single cell can cause catastrophic failure of the battery as a whole; it is therefore important to know the condition of the battery at all times.

VRLA cells are sealed, therefore the traditional method of measuring the specific gravity of the electrolyte to estimate the capacity of the individual cell (in itself not very accurate) is not possible; the only certain method of determining to what extent the battery is capable of supporting its critical load is by autonomy (discharge) testing the battery as a whole. However most installations have to be shut down during the testing to avoid possible damage to their critical loads and this can be problematical to the services they supply.

In addition, discharge testing in large standby battery systems, particularly if they have more than a single string, is expensive, disruptive and wasteful of energy and resource. A meaningful discharge test will require the disconnection of the battery or individual strings from the critical load and connection to a DC load bank, and will take several hours to carry out. Recharging to a point where the battery could perform to specification in the case of a mains failure could mean that the whole operation could take in excess of 24 hours *per string*. A major consideration to take into account when relying on an annual discharge testing for battery reliability is that it is only valid on the day of testing; it is not unheard of for the recharge to cause cell failure modes to develop, so a few days after the test the condition of the battery is once again unknown.

To avoid the high cost and disruption these tests entail, less invasive instrumentation methods which attempt to determine battery condition on-line without disconnection from the load have been developed and are now widely available. The aim of these systems is to provide enough information about the battery to detect any incipient failures, enabling the extension of the service life of the battery and preventing catastrophic failure during a power outage.

The most effective on-line methods to date are the Ohmic measurements of internal DC resistance or AC impedance. Resistance and impedance however have been shown not to be totally reliable in detecting standby battery deterioration until the capacity has reduced to perhaps 70-60% of the specified capacity [2].

Since all standby battery manufacturers recommend that standby batteries are changed out when the capacity has deteriorated to 80% of the original specified capacity, the ultimate aim of battery testing is to reliably detect a fall in capacity from 100% down to 80% capacity, i.e. *before* the deterioration has advanced enough for the battery to be unreliable in service.

It is clear that a fresh approach is necessary to reliably detect the *onset* of battery deterioration, rather than detecting the condition after deterioration has become advanced.

The electrical equivalent circuit

In 1883 Thévenin established that in ‘black box’ conditions, all complex electrical activity can be approximated by a simplified representative electrical circuit. The standard circuit for a lead-acid cell is known as the Randles equivalent circuit.

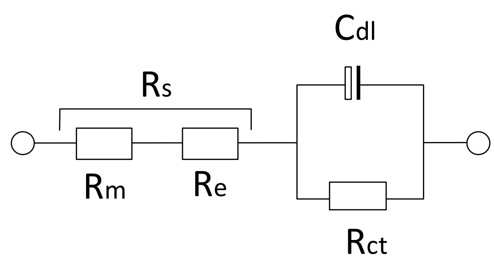


Figure 1: The Randles equivalent circuit for a lead-acid cell

The well-known circuit in figure 1 is the simplest that can approximate the actions of an electrochemical cell under charge or load. **Rm** represents the metallic resistance of the plates and connections, **Re** is the electrolyte resistance; **Rm** and **Re** cannot be separated by testing at the cell terminals, so they are normally added together and shown as **Rs** (series resistance). **Rct** is the charge transfer resistance, due to plate-electrolyte ion transfer limitations; **Cdl** is a capacitance created by a double layer of ions at the plate/electrolyte interface. The electrochemical voltage and current generator is often omitted.

Resistance, Impedance and Conductance in lead-acid cells

The first cardinal parameter in the Randles circuit is resistance. Figure 2 shows the progress of the actual impedance of a battery in service. The dotted green line is the initial impedance and the purple line the critical alarm level. It can be seen from the graph that the impedance of the battery, which has been in service for several years, had not changed significantly in the years before the start date of the graph (a little less than 5%). The significant rise in impedance (the yellow dotted line) can be seen to be late in the deterioration process and only a short time before the end of life occurs.

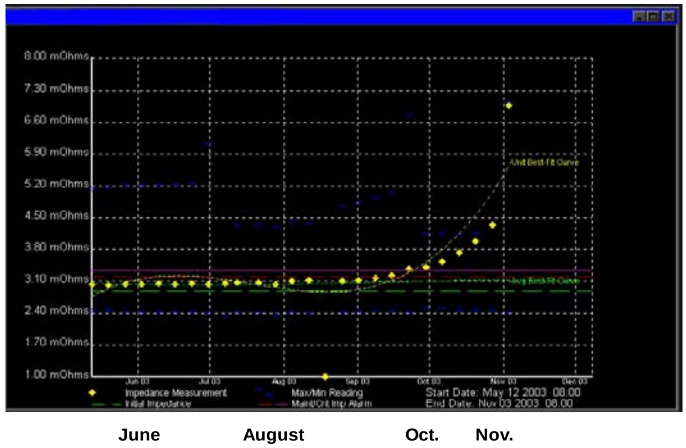


Figure 2: In-service battery impedance at end of life Graph courtesy of Btech Inc.

It is normal in the industry to set the alarm level at 130-150% above initial impedance to avoid false alarms; in the case of the battery in figure 2 this would mean that the time between alarm and total failure would be around 2-3 weeks. Whether resistance (DC) or impedance (AC) is the preferred method of testing, the characteristics of both virtually always follow the same well-known pattern over the life of the cell (figure 3).

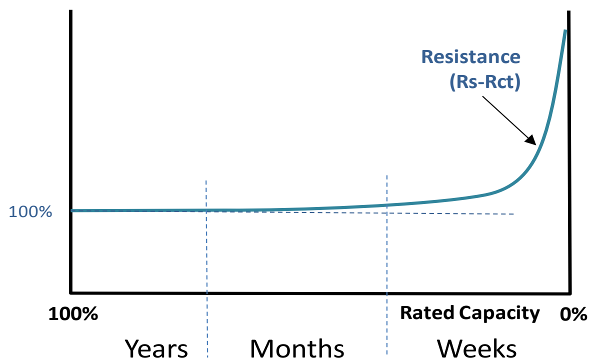


Figure 3: resistance/impedance curve of a lead-acid cell over service life

Standby battery testing methods

Resistance: Apart from discharge testing, the two established methods for battery testing available in the standby industry today are DC resistance, which has been used in testing batteries for several decades, and AC impedance; both have been in use in commercial instruments for over 15 years. On-line resistance testing (of which more later) consists of a single extended DC pulse of current being drawn from the cell; it concentrates on the Ohmic value of the series resistance only. Impedance draws current in a series of pulses at a set frequency; this does include a capacitive effect, but does not look any further into the individual component parameters than resistance testing does. Claims by the advocates of the resistance method that single frequency impedance testing obscures important information may therefore have some substance [3, 4]; however DC resistance testing ignores the same information.

Conductance is suggested as a better descriptor of the ability of the cell's capability to deliver current than resistance and impedance but conductance is simply the reciprocal of resistance (1/R); therefore it is actually the method of resistance testing that is important; conductance just describes resistance in a different way.

Admittance has also made a late appearance on the scene described as a 'new' parameter but since admittance is the reciprocal of impedance the same rules apply as those for conductance.

To determine the truth about the various claims for impedance, resistance and conductance, the Electrical Power Research Institute (EPRI) conducted a comprehensive two-year program of research into the effectiveness of impedance and resistance/conductance testing of lead-acid batteries; despite claims by various commercial instrument companies their report [2] concluded that there is no direct correlation between State of Health (SoH) and resistance/impedance, particularly in the initial stages of capacity loss, and no significant difference in effectiveness between resistance, impedance and conductance.

In addition, the extensive data collected throughout the EPRI project showed that resistance, impedance and conductance indicators are not totally reliable until deterioration has reduced the capacity of the cell to 70-60% of nominal.

Capacitance

The second major parameter of the Randles circuit is capacitance. The characteristic of a capacitor is that it exhibits its maximum rate of change of voltage as it begins to discharge. Figure 4 shows the characteristic voltage curve of a capacitor discharging through a resistance. In this representation the current of the circuit will reduce as the voltage of the capacitor reduces.

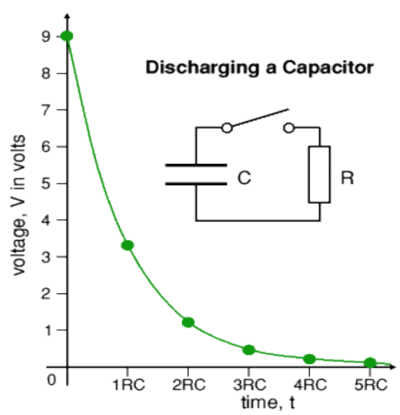


Figure 4: Characteristic voltage curve of a discharging capacitor (Graph: Schoolphysics.co.uk)

How does capacitance behave in a battery? In order to explain this we need to identify the two major capacitances present in the lead-acid cell.

Capacitor action in lead-acid cells

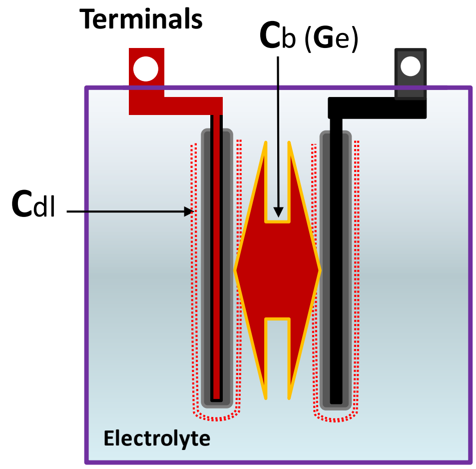


Figure 5: The two most significant capacitances occurring in a lead-acid cell, Cdl and Cb (Ge)

Double layer capacitance (Cdl) (figure 5) is a well-known phenomenon present in all batteries and supercapacitors [6] and figures 6A, B and C illustrate the principle.

As an example, if a positively polarised plate is immersed in an electrolyte solution (figure 6A), chemical and thermal action attracts opposite polarity ions and establishes a diffusion layer between the plate and the electrolyte, with *negative* ions being attracted and adsorbed, creating a thin film on the surface of the positively charged plate.

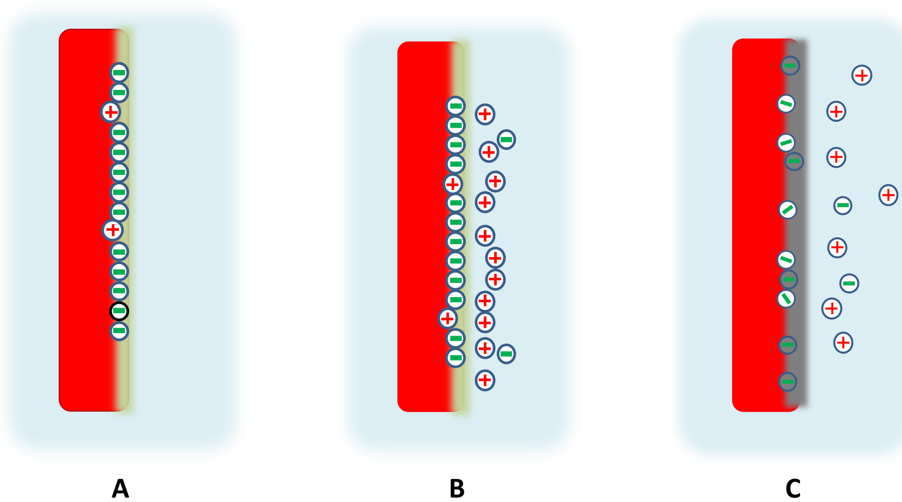


Figure 6: Double layer capacitance in lead-acid cells

Attracted by the negative adsorbed layer, a layer of *positive* polarity ions form a second layer at a few nanometres distance from the diffusion layer (figure 6B); these two layers are known as the Helmholtz double layer capacitance (Cdl) or surface capacitance.

As the cell ages, or failure modes develop, sulphation, corrosion or loss of electrolyte replaces or weakens the plate's adsorbed layer and the attraction between this and the second layer of ions (figure 6C) is reduced. With less force of attraction, the second (now weaker) layer of ions now forms further from the active plate material. Since the magnitude of the capacitance depends directly on the area of the plates (layers) and the distance between them, this has a two-fold effect: the capacitance reduces due to reduction in active plate area, and the increased distance between the layers itself causes a further reduction.

Double-layer capacitance is therefore an extremely sensitive indicator of the State of Health (SoH) of the cell, exhibiting its greatest change in the early stages of capacity loss. In testing therefore it is Cdl which is the critical indicator at the onset of deterioration whereas resistance manifests more strongly in the latter stages.

The second of the two main capacitances shown in figure 5 is the electrochemical generator, often identified as the **bulk capacitance, C**b [5]**,** in the form of two adjacent metallic plates in an ion charge transport medium. This is not actually a capacitance but, in practical terms, an electrochemical voltage and current generator, (**G**e). In the Randles diagram Cb (Ge) is often ignored, or represented by a voltage source icon; in testing, its behaviour can be likened to that of a capacitance several orders of magnitude larger than the double layer capacitance.

The double-layer capacitance is therefore a static field phenomenon and the 'bulk capacitance' is an electrochemical one. Cdl, as a true capacitor can react instantaneously to a discharge, whereas Cb, as a chemical reaction, is slower to react. It will be shown that the electrochemical generator will only begin to generate current when Cdl is exhausted; this is the reason many discharges have the well-known 'coup-de-fouet', which occurs when there is not sufficient energy in Cdl to support the discharge current until the electrochemical generator is fully operational.

In theory then, if we superimpose the capacitance behaviour onto the resistance graph (figure 7), we get an idealised equivalent circuit component model for the life of a lead-acid cell that looks like this:

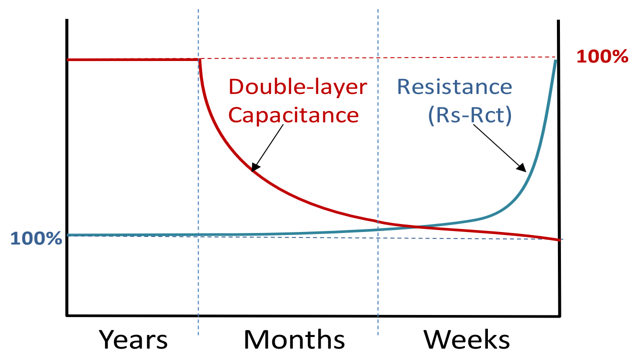


Figure 7: Idealised lifetime resistance and capacitance characteristics for an L-A cell

In the idealised model in figure 7, a sudden fall in capacitance represents the onset of serious deterioration. The sharp corner at inception would not normally occur in practice, nevertheless a significant change in the capacitance Cdl, several orders of magnitude greater than that of resistance, is exhibited in the early stages of deterioration.

The Detection of Incipient Capacity Loss

In order to understand why the cell parameters are important, the electrical characteristics of a cell under test must be understood, and to do this the Randles circuit must be expanded to include the electrochemical generator [5].

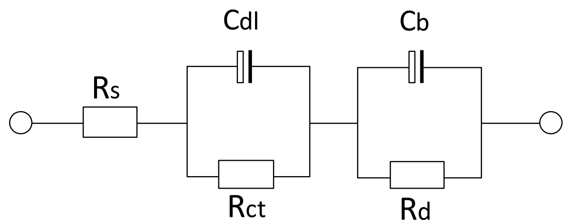


Figure 8: Expanded equivalent circuit for a lead-acid cell

In this expanded equivalent circuit shown in figure 8, **Rs** is the series resistance (Rm + Re), **Rct** is the plate to electrolyte charge transfer resistance, **Cdl** is the double layer capacitance, **Rd** is the internal self-discharge resistance (in the order of kilohms) and **Cb** is the electrochemical generator, shown as a bulk capacitance.

Following the Scott patent in 1997 [7], several methods of identifying the individual Randles components of an in-service cell commercially have been published [8,9]; they are all however fairly complicated and little work has been done commercially to explore the actions of the individual measured parameters.

A simple test can be used to illustrate the principle; the DC test shown in figure 9 has been used for several decades both in the laboratory and in commercial instruments to identify series resistance. Until now resistance has been the only one of its response mechanisms to have been recognized or investigated in the context of the standby battery industry; however if the response mechanisms of the test are understood, all the parameters of the expanded Randles circuit can be identified from it.

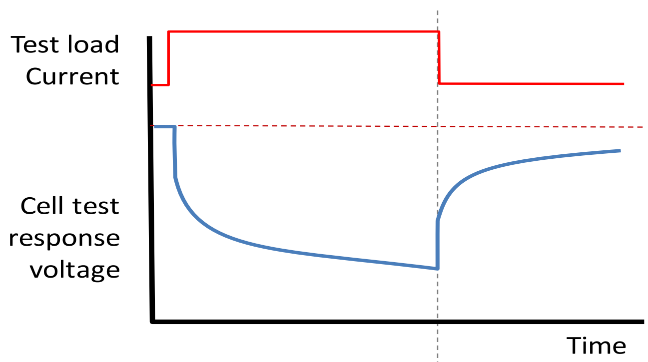
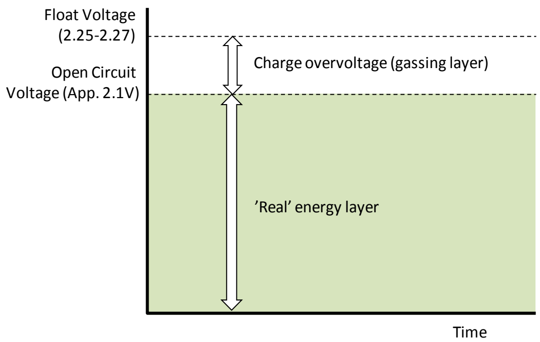


Figure 9: Testing an on-line lead acid cell

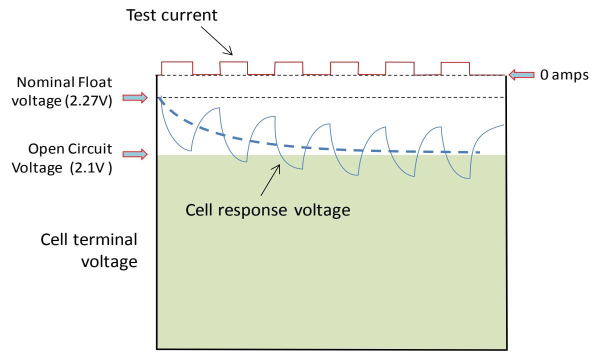
For this test the cell is assumed to be in-circuit, under float charge. A fixed amount of steady-state DC current is drawn from the cell under test in a step change and the response voltage from the cell is measured and recorded. Despite being under float charge conditions, the cell's voltage response characteristic can be observed to show very little difference between voltage response under load and that of recovery (current-on and current-off). The recovery characteristic is not so affected by the gassing layer, however the response under load is shown here for clarity.

Test current under float current test conditions: Since all resistance and impedance measurements rely on the cell's voltage response to a current stimulus, for the test to be reliable the current used to stimulate the cell response should be of sufficient magnitude.

This is not just to overcome system noise or the influence of the float current on the test, but to derive a response from the electrochemical energy layer of the cell. The charge overvoltage, or gassing layer (figure 10A), is the difference between the cell's open circuit voltage and the float voltage set by the charger. The float current passes through all the cells in the string, and it is therefore influenced by all the cells, not just the cell under test. The float charge overvoltage therefore cannot always be relied upon to indicate the true condition of the cell under test. Testing with a low current means that the voltage response comes mainly from the overvoltage and not from the cell (figure 10B).



A



B

Figure 10 A: Float charge overvoltage   Figure 10B: Ineffective low-current testing

Low current testing therefore cannot always be considered reliable, particularly on larger cells or in above average noise/ripple conditions. AC testing is even more vulnerable than DC for the same test period, as the test current is interspaced 50/50 with off periods therefore the effect of the test current on the cell is halved. For this reason when on float charge it is also not reliable to use an AC current signal oscillating above and below the float voltage, particularly since the AC current in this case, being rated at peak-to-peak, the effective current in either direction is only 0.7 x 0.5 of that.

Float current is important; as the cell becomes fully charged, the voltage generated from the electrochemistry of the cell itself limits the charge current; this is often referred to as the 'back EMF', a term familiar in electric motors. At the end of the charge proper, a healthy cell will have a higher natural voltage and the float current will be lower for the same charger-set float voltage than that of a deteriorating cell, therefore float current is a good indicator of battery condition.

The test current must therefore be of sufficient magnitude to eliminate the 150 or so millivolts of overvoltage before the cell itself can respond.

During the DC test, as the current is actively drawn from the cell, the voltage response is actually composed of different rates of change and these distinct stages can be differentiated as follows:

The three stages of test voltage response

The voltage response of the cell under the stimulus of the test load current shown in figure 9 can be shown to be derived from three separate component effects:

1. Series resistance, Rs

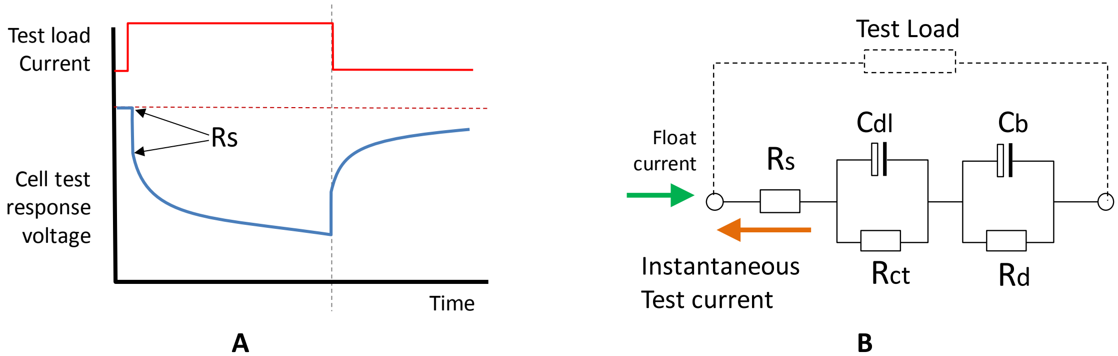


Figure 11: The vertical section of the voltage response proportional to internal resistance

The first component is the series resistance **Rs**. At the instant of applying the test load the current reverses from float (charge) current to test (discharge) current. The initial drop in voltage seen in figure 11A is the potential difference that previously existed across Rs (figure 11B); the current from this point is supplied only from Cdl and not from the electrochemical source, Cb. In this first stage the voltage response can be assumed to be vertical (figure 11A) and the magnitude of the vertical drop (and vertical recovery at the end of the test) divided by the test current gives an accurate value for the series resistance of the cell, **Rs**.

2. Double layer capacitance, Cdl

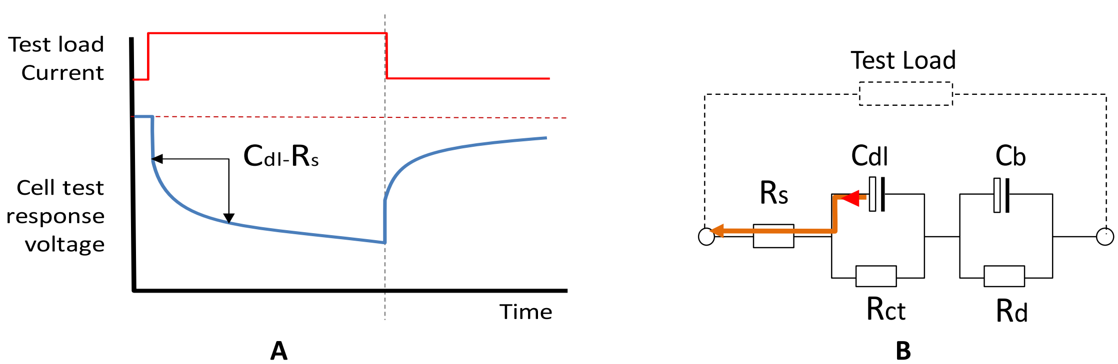


Figure 12: The Cdl discharge curve

The second component gives the curve shown in figure 12A. This is the effect of Cdl discharging through Rs (figure 12B). As the test current, the magnitude of which is controlled by the test instrument, becomes steady state Cdl begins to discharge through Rs and this produces the characteristic voltage curve of a capacitor discharging through a resistance.

The current used in this type of test should be substantial, but will not be of sufficient magnitude to impact significantly on the bulk capacitance (Cb), which can be seen as in the order of 10^5F. In fact if the test current is too high i.e. in the region of 1C, the cell response will begin to exhibit a Coup de Fouet [10], since the electrochemical generator is not instantaneous in delivering current (Cdl must be discharged first) and the energy in Cdl will be insufficient to supply the magnitude of the load current.

3. The bulk capacitor (Cb/Ge)

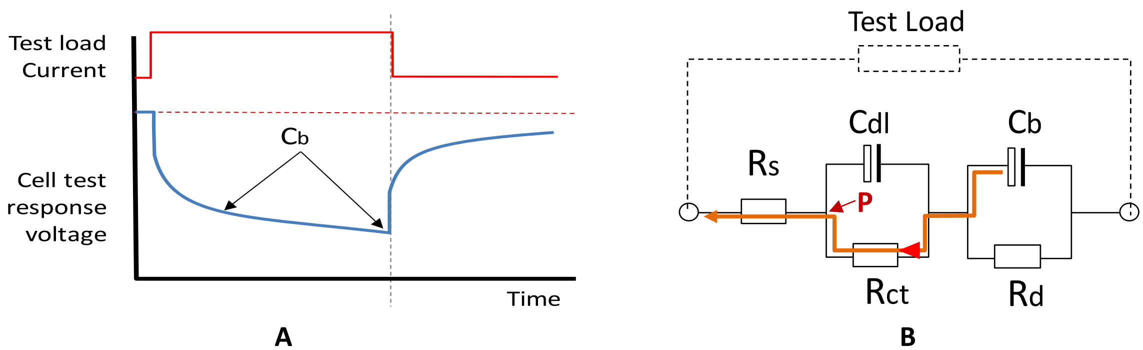


Figure 13: The bulk capacitance linear response section

When Cdl has discharged to the point that its voltage is the same as the potential of Cb at point P (figure 13B), Cb becomes the sole supplier of current and Cdl plays no further part in the test response. The voltage response (figure 13A), now exhibiting the discharge of the (very large) bulk capacitance through a resistance (Rs + Rct), reduces very slowly, more a downward drift and, for the purpose of this test, can be considered linear.

Since Cdl is orders of magnitude smaller than Cb and is totally dependent on the health of the plates and electrolyte, it is far more sensitive to changes in the electrochemistry of the cell than Cb and these changes can be identified in the test voltage response. Tests, verified by discharge testing, on Hawker VRLA monoblocs at various stages of capacity loss are shown in the two graphs in figure 14.

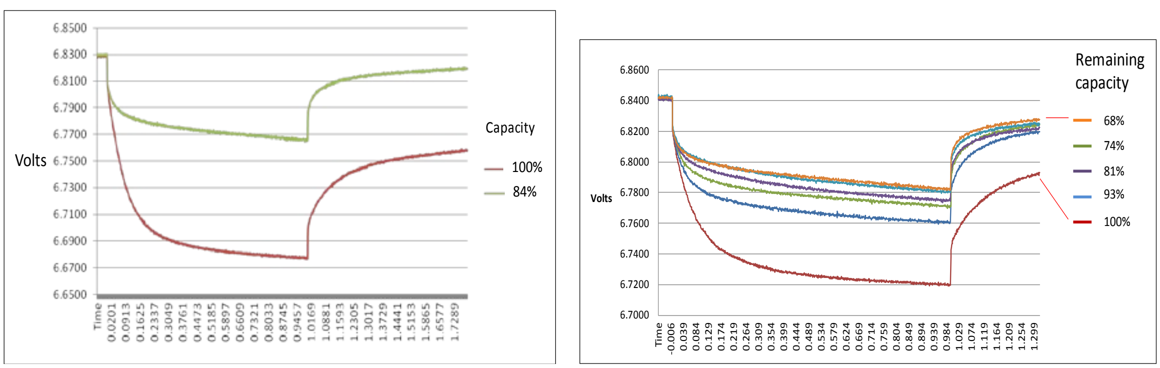


Figure 14: Reduction of depth of Cdl-Rs curve of VRLA monoblocs at different capacities

The effect of the double-layer capacitance: It can be seen from figure 14 that the vertical portion of the test voltage proportional to the series resistance remains almost identical at each of the early stages of capacity loss. Also, the part of the response voltage equating to Cb can be considered linear and will remain parallel at the various capacities from 100% capacity down to approximately 30% capacity.

The reduction in the depth of test voltage profile in the two examples in figure 14 is due to the reduction of the Cdl discharge curve, which is directly proportional to a reduction in double-layer capacitance.

Once the structure of the test voltage response is understood the information it provides is invaluable in predicting deterioration during the early stages of capacity loss.

The effect of series resistance: The early changes in test response due to the reduction of Cdl in the early stages of deterioration can be compared to the latter stages of deterioration in the two examples in figure 15, from a remaining capacity of just under half down to exhaustion. It can clearly be seen that the increase in depth of the voltage response profile is due to the increase in Ohmic resistance.

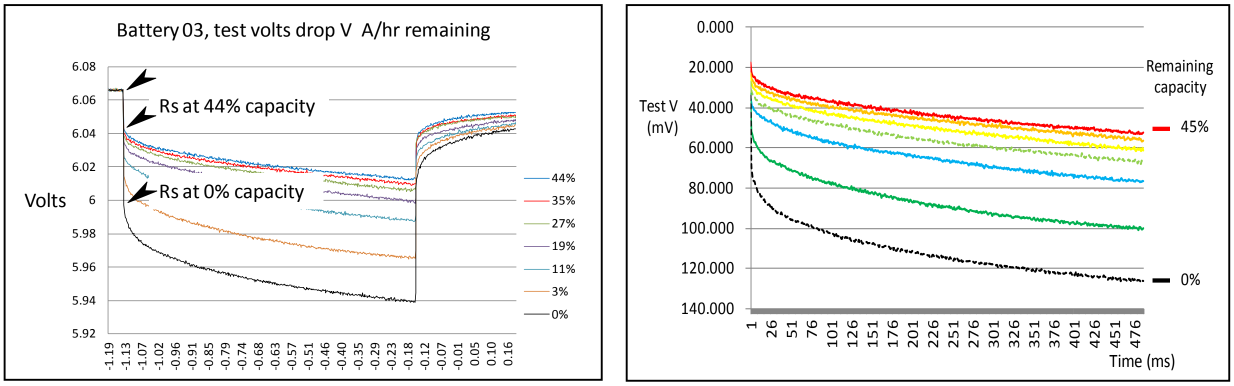


Figure 15: Increase in test response voltage due to increase in Ohmic resistance

Our tests showed that there is also a detectable change in the slope of the linear portion as the cell approaches exhaustion, indicating that the energy in the bulk capacitor (Cb/Ge) has been reduced to the extent that it can now be affected by the test current.

Combined capacitance/resistance behaviour

The theorised test voltage profile from figure 11 is here brought forward as figure 16A, which can now be compared to the actual test total voltage profiles of both the early and late stages of deterioration combined in figure 16B.

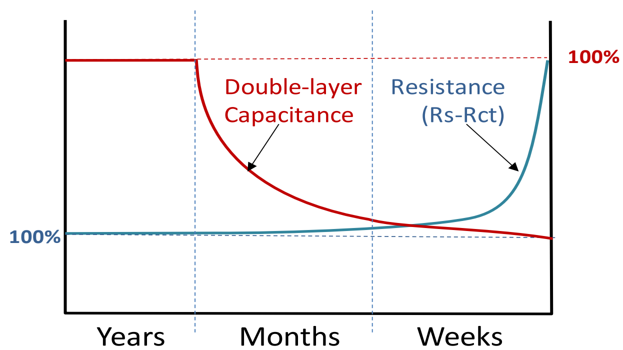


Figure 16A: Posited resistance and capacitance profiles

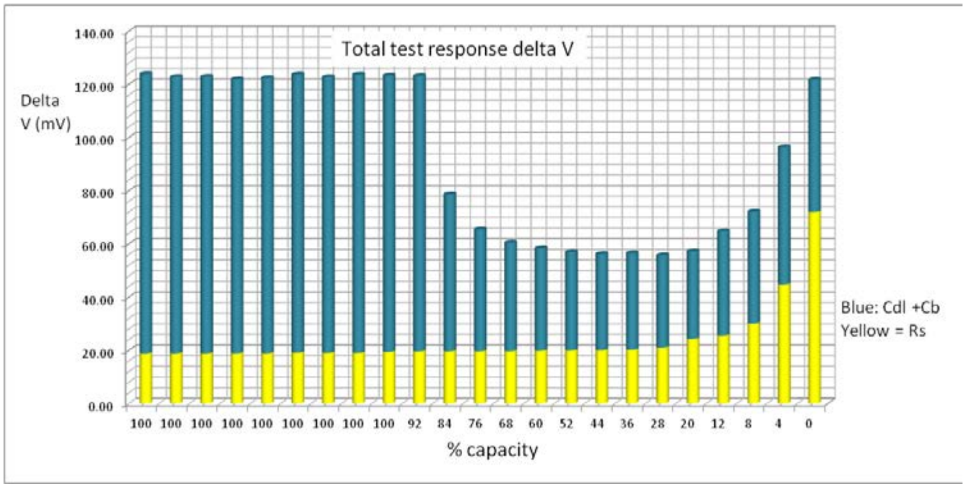


Figure 16B: Capacitance-resistance test voltage deltas from VRLA monobloc #2

Figure 16B is the total test voltage response delta from test inception to termination of current. The resistance characteristic (in yellow) becomes more reactive as the jar moves towards exhaustion. The capacitance and resistance test values can be seen to be proportional to the theorised behaviour (16A) of capacitance and resistance over the life of the cell.

The fall in response voltage (initially between 100% and 92% capacity) is due to a reduction in Cdl (blue); whereas the subsequent rise is due to an increase in series resistance. The slightly flattened middle portion of the test voltage curve is caused by the crossover of the falling capacitance and the beginning of the rise due to resistance.

Sulphation

Both plates in a lead-acid battery naturally turn to lead sulphate in the process of a discharge; however the condition is reversed when the cell recharges. Sulphation can also take place prematurely if the cell is undercharged or left in a discharged state for any length of time, or the float charge voltage is incorrect for the cell temperature (figures 17A and 17B).

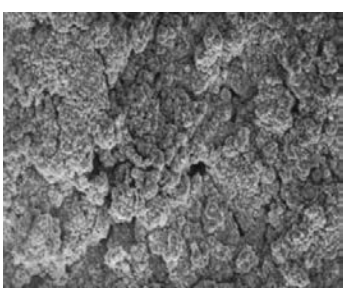


Figure 17A: New plate, with no sulphation.

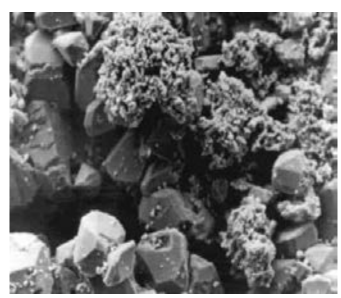


Figure 17B: Plate from undercharged cell after less than one year, with pronounced sulphation.

If detected early enough the condition can be reversed by one or more high current charge/discharge cycles; if not detected the lead sulphate crystals gradually grow and harden and the condition becomes irreversible, insulating the plates, which prevents current flow and causes the cell to fail prematurely.

Resistance/impedance testing will not detect sulphation until the condition is well advanced; however the capacitance is sensitive enough to detect sulphation in the early stages, allowing time for remedial action to be taken.

Academic validation

In order to confirm our work, Heriot Watt University in Edinburgh, one of the UK's leading technical universities, was asked to design a predictive computer model based on the Capacitive-Resistive system and the expanded battery circuit model, and to generate predictive capacity loss graphs for each of the test cells at various capacities, without reference to actual test data [11].

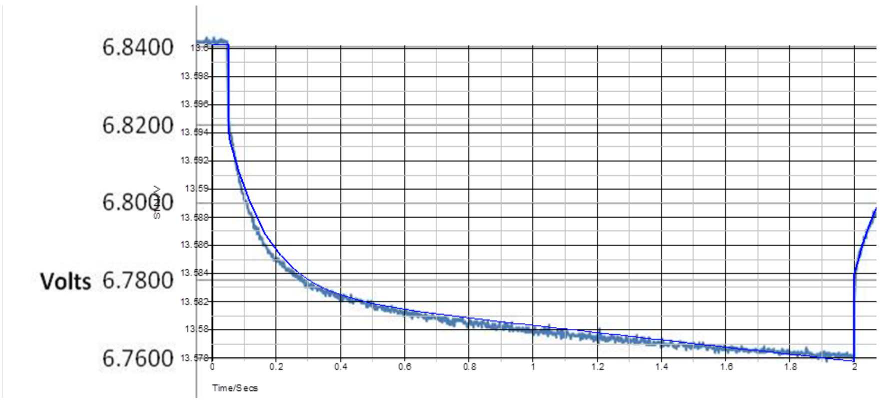


Figure 18: Computer generated model overlaid on actual test data (dark blue CGM, light blue data)

Figure 18 shows a test on a Hawker monobloc at 82% capacity. A predictive computer model of the test voltage was constructed by Heriot Watt University using the same test current for the model as for the actual tests.

The model predicted test data for 82% were then physically overlaid on the actual test results and the almost exact fit (less than 3% deviation) of one to the other confirms the accuracy of the deterioration prediction process. The actual capacity was confirmed by discharge testing.

The University of Saint Andrews evaluated the (electro) chemical processes of the Capacitive-Resistive system. Their report confirms the description of test responses and verifies the system from the chemical standpoint. Their work on the system is continuing for other battery chemistries.

Summary

Tests on many different sizes and types of VRLA type monoblocs together with flooded Plantè and OPZ cells have confirmed that the analogue of capacitance in the Cdl-Rs discharge curve (figure 12) is the prime indicator of the early stages of deterioration in standby batteries. Measurement of resistance on the other hand can identify the less frequent failure modes which are purely resistive and is certainly useful in indicating relatively advanced capacity loss.

The Capacitive-Resistive system utilises the cell's capacitance to detect the early stages of cell electrochemical deterioration and capacity loss. Resistance is integrated with capacitance to reinforce the analysis and detect the latter stages of capacity loss or purely resistive failures modes, such as metallic plate-post connection problems. The two components together give a much clearer picture of the progression of cell deterioration and loss of capacity than has been the case in the past using purely resistance or impedance.

The proposed system detects a very measurable change in the early part of a failure mode or end-of-life, which is several orders of magnitude more than resistance and is a significant step forward in the prediction of battery State of Health (SoH).

This advance enables the first 10-20% of electrochemical capacity loss in on-line cells to be accurately predicted. This answers one of the most important criteria in the management of standby battery systems; the ability to predict end-of life *before* the condition becomes advanced enough to render the battery unreliable.

The Capacitive-Resistive system is being developed into a new instrument due to be completed later this year.

References

[1] p1; Dr D.O. Feder: Journal of Electrochemistry; 2008

[2] p2,3; EPRI: Stationary Battery Monitoring by Internal Ohmic Measurements 1002925 Final Report December 2002

[3] p3; Glenn Albér: Ohmic measurements, the history and facts; position paper 2003

[4] p3; Dr Robert S Robinson, Channel D Corporation: On-line Battery Testing: A Reliable Method for Determining Battery Health?

[5] p4; Gould et al: New Battery Model and State-of-Health Determination Through Subspace Parameter Estimation and State-Observer Techniques, IEEE TRANSACTIONS ON VEHICULAR TECHNOLOGY, VOL. 58, NO. 8, OCTOBER 2009

[6] p5; B. E Conway: Electrochemical Supercapacitors: Scientific, Fundamentals, and Technological Applications, Kluwer, New York (1999).

[7] p6; N D Scott: Electrochemical deterioration test method and apparatus; Patent GB98/02949; 1997

[8] p6; Keith S Champlin: Method and apparatus for measuring complex impedance of cells and batteries, US6, 002, 238, 1998

[9] p6; Chul Oh Yoon et al: Method and apparatus for measuring battery capacity using voltage response based on pulse current, US6, 118, 275; 1998

[10] p10; HUA Shou-nan et al: The coup de Fouet (CDF) of the VRLA battery and the relationship between the CDF and the battery capacity, School of Chemistry and Chemical Engineering, Shandong University, 2009

[11] p11; Dr. Qi Shang and Dr. Matthew Dunnigan: Report on electrical modelling of VRLA battery and parameter estimation for state of health monitoring in UPS applications, HWU 2006, 2014