A new pH phenomenon to predict polarity reversal in Lead-Acid cells.

J. Mooney[1], A. Alaswad[1] and A. Cruden[2]

[1]School of Engineering and Computing, University of the West of Scotland, United Kingdom

[2] Engineering and the Environment, University of Southampton, United Kingdom

Abstract

This paper discusses new experimental work investigating the change in pH of the electrolyte of individual cells in Lead-Acid batteries during discharge with a view to predicting cell polarity reversal and thereby pre-empting potentially catastrophic failure in batteries. The discharge tests were carried out on batteries which were classified as ‘new’ and ‘aged’ as a means of indicating their state of health. A new pH phenomenon has been recorded for the first time in this paper as evidenced by experimental results including measurement of half-cell potentials. The trends observed during the discharge tests could be used as additional means of indicating impending cell reversal in series connected Lead-Acid cells.

Keywords: Lead-Acid, pH, Cell, Voltage and Condition Monitoring, batteries, energy storage.

Corresponding author: Abed Alaswad

Abed.alaswad@uws.ac.uk

1. Introduction

The growing need for sustainable and secure energy along with the climate change concerns have led to increasing interest in renewable energy technologies in the last two decades [1], consequently, many electrochemical systems like batteries and fuel cells have been turned into attractive solutions to store the obtained energy effectively in stationary, portable and transport applications [2,3]. The widespread adoption of such systems as a means of providing both motive and static power will require diagnostic systems capable of supporting these systems during their service life. A means of condition monitoring and ultimately end-of-life prediction is desirable for the continuing successful penetration of these systems into the transport and static power markets. This paper describes a means of predicting degradation and failure of an electrochemical lead acid cell based on the measurement of the pH of the cell electrolyte. Despite being invented in the mid 1800's, lead acid batteries are the most widely used rechargeable systems [4]. Lead acid (Pb-acid) batteries are the most mature rechargeable battery technology, with over 150 years of development behind them. Even today in the 21st century, lead-acid batteries share about 50% of the rechargeable batteries market, and research is continuous to enhance their performance [5, 6]. That is due to the combination of low-cost, versatility and the excellent reversibility of the electrochemical system, in spite of having a poor energy density, 18 to 34 Wh/kg, when compared to other battery types such as Lithium-ion with energy densities of 130 to 255 Wh/kg [7,8].

The active materials in Lead-Acid batteries include the positive and negative electrodes and the electrolyte, lead and lead dioxide, which are the active materials on the battery’s positive and negative plates, respectively, during discharge these react with the distilled water and sulphuric acid mixture, which forms the electrolyte, to generate electrical current [9]. However, it was reported that Ohmic resistance readings cannot replace a discharge test to determine percentage capacity or ampere-hours capacity [10]. However, Ohmic measurements can be used as a trending tool over time in field service to identify weak cells that may require further evaluation.

The electrolyte is an active component in the cell chemistry, and the electrolyte concentration, usually expressed in terms of specific gravity, varies as the cell is charged and discharged as shown in Table 1.

Table 1: Sulphuric acid properties [11].

The electrolyte concentration changes during cell operation (see equations 1, 2 and 3) and correspondingly the pH of the sulphuric acid electrolyte varies according to the state of charge and hence the cell voltage also varies. The chemical reactions relating to a Lead-Acid cell according to [12] are listed in equation 1:

$$Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-}(aq) \leftrightarrow 2PbSO_4(s) + 2H_2O \qquad (1)$$

The corresponding half-cell reactions during discharge are listed in equation (2- 3):

At the positive electrode (electrochemical cathode):

$$PbO_2(s) + 3H^+ + HSO_4^- + 2e \leftrightarrow PbSO_4(s) + 2H_2O(aq) \qquad (2)$$

At the negative electrode (electrochemical anode):

$$Pb(s) + HSO_4^- \leftrightarrow PbSO_4(s) + H^+ + 2e \qquad (3)$$

In the range of pH relevant to the operation of a lead-acid battery, that is -1.0 < pH < 1.0, the sulphuric acid dissociates into hydrogen and bisulphate ions. And the HSO_4^- ion is predominant across this range of pH [13]. The relationship between the electrolyte pH and the theoretical cell voltage for a Lead-Acid cell can be expressed in terms of equation 4, the Nernst equation [14].

$$E = E^0 + \frac{RT}{nF} ln(a_{H^+})(a_{HSO_4^-}) \qquad (4)$$

Where:

E is the theoretical open circuit cell voltage (volts).

E^o is the ideal or reversible cell voltage (volts).

R is the universal gas constant (KJ/kg.K).

T is the absolute temperature (K).

n is the number of moles of electrons transferred in the reaction.

F is Faraday’s constant (96485.3 C/mol).

a_{H^+} and $a_{HSO_4^-}$ are the activities of the hydrogen and bisulphate ions respectively. Note that the pH of the electrolyte can be theoretically determined by using equation 5 [15]:

$$\text{pH} = -\log_{10}\left(a_{H^+}\right) \qquad (5)$$

From equation [5] it can be seen that pH is a function of activity and as the activity of H^+ increases, pH decreases. Furthermore from equations 4 and 5 it can be seen that there is a relationship between theoretical cell voltage and the pH of the sulphuric acid electrolyte. However, the Nernst equation is based on equilibrium conditions where the net current flow into the cell is assumed to be zero. Under actual operating conditions the relationship between pH and the cell voltage cannot be determined using equation 4 and 5, as the cell is not in a state of equilibrium when it is undergoing charging or discharging as the net current flow is no longer zero.

In practice, the passage of any finite amount of electricity results in a certain degree of irreversibility as some of the electrical energy is dissipated as heat either via the internal resistance of the cell, or at the cell electrodes where application of a potential difference is required to drive the current at the desired rate. The cell voltage under an external load is always smaller than the open circuit voltage, so that only part of the thermodynamically available work can be utilized [16].

The concept of using measurement of battery electrolyte pH has been previously reported by Bayuomy [17], is this case the measured value of electrolyte pH was used as the input to a charge control system in a photovoltaic hybrid power system which incorporated lead-acid batteries.

2. Experimental Work

A widely used method of assessing ‘wet cell’ lead-acid battery condition is the measurement of the electrolyte specific gravity. The measurement of electrolyte specific gravity almost invariably involves the use of an external hydrometer by physical sampling of the battery electrolyte. This method is quick and convenient for a discrete measurement of a single cell, however continuous monitoring is difficult to implement, particularly in a battery system with a large number of cells.

After reviewing various methods of monitoring battery condition it was decided to investigate measurement of electrolyte pH as a means of determining battery condition. This method is considered to be appropriate for the following reasons.

1. Electrolyte pH is a function of activity and hence acid concentration, and is therefore similar to specific gravity insofar as the state of charge could be approximated by measuring the pH of the electrolyte.
2. Continuous measurement of electrolyte specific gravity is difficult to achieve in practice whereas electrolyte pH can be measured on a continuous basis offering the prospect of ‘on line’ monitoring of battery cell condition.

A series of discharge test were undertaken on a number of Lead-Acid batteries to monitor the variation of the pH of the electrolyte during the discharge of the battery. The tests were undertaken using 6-cell automotive Starting Lighting and Ignition (SLI) batteries and individual Plantè cells. Figure 1 shows the battery test facility. A 6-cell automotive SLI battery can be seen next to a wooden crate which contains a Plantè cell undergoing a discharge test. The two 12 volt vehicle light units were used as loads to discharge the SLI batteries, wire-wound resistors were used to discharge the Plantè cells.

Figure 1: Battery testing facility.

Figure 2 shows the sensor arrangement used, the pH sensor is located in the cell using a simple fixture to position the pH sensor in the cell electrolyte, approximately in the centre of the cell. Frequent checks were made on the test instrumentation and calibration checks were undertaken using buffers solution to ensure the accuracy of the pH meters.

Figure 2: Arrangement for locating pH sensor in Plantè cell.

The change in condition of a battery during the discharge test, voltage, current and electrolyte pH was measured using National Instruments LabVIEW © software. The voltage current and electrolyte pH were monitored and recorded during the discharge test using a PC based measurement system. Using a LabVIEW© Virtual Instrument (VI) acting both as a monitor and data logger, with the captured data being stored in a file format which can be downloaded to a spreadsheet for subsequent analysis. Figure 3 shows the VI developed to measure cell voltage, current and electrolyte pH during a discharge test on a SLI battery. A pH probe was inserted into one of the 6 cells, and recorded electrolyte pH, along with terminal voltage and current was measured as the battery was being discharged by an external load consisting of two automotive light units.

Tests were carried out on both ‘aged’ and ‘new’ cells, using both Plantè cells and SLI batteries. The pH data returned from these tests had a notable feature in that there was a clearly discernible disturbance in the pH reading during the discharge test, illustrated in Figure 3. It should be noted that in all of the discharge tests the cells are discharged well beyond the cut-off voltage [18].

Figure 3: LabVIEW© Front panel for pH monitoring.

Figure 4 shows the results of a discharge test on a SLI battery in an ‘aged’ condition. The pH of the electrolyte of one of the six cells is being measured along with the battery voltage and current. At about 4000 seconds in the discharge test a ‘disturbance‘ in the measured value of pH takes place. From Figure 4 it is clear that the measured value of pH undergoes a ‘disturbance’ at between 4000 and 6000 seconds in the discharge test. At about the same time the battery voltage and current undergoes a discernible decrease, the battery voltage decreasing by approximately two volts. As the battery under test was a Starting, Lighting and Ignition (SLI) 6 cell battery it was difficult to measure the voltage of the individual cell in which the electrolyte pH was being measured.

Figure 4: Discharge test on SLI battery, showing battery voltage (Volts), discharge current (Amps), and electrolyte pH.

Subsequently, during later testing, individual cell voltage measurement was achieved by connecting a Plantè cell electrically in series with a SLI battery, effectively resulting in a 7 cell battery. The Plantè cell was connected to the SLI battery to give it the highest potential with respect to circuit ground. It was arranged such that the SLI battery was fully charged, however, the Plantè cell was deliberately not fully charged in order to ensure that it would the ‘weakest’ cell of the 7 cell in series. The combined Plantè-SLI battery was then discharged and continued until the Plantè cell was driven into voltage reversal. The results of one of these tests are shown in Figure 5. The pH disturbance at about 300 seconds in the discharge test, with the cell reversing polarity at about 500 seconds is displayed. It can be seen that the pH disturbance occurs before the Plantè cell voltage falls below zero volts. The figure also shows that the cell voltage declines below zero i.e. reverses and then settles at approximately negative 0.4 volts, where, at this point the Plantè cell is now effectively being charged by the SLI battery.

Figure 5: Plantè cell discharge test leading to cell reversal, showing cell voltage (Volts), discharge current (Amps) and cell electrolyte pH.

The discharge test described above replicates a common failure in SLI batteries that is the reversal of a single cell, effectively rendering the battery unserviceable. However, a failed cell in a long string of series-connected batteries could be driven into reversal without rendering the entire battery string unserviceable, the reversed cell absorbs power from the other batteries in the string which in turn results in heat generation in the failed cell and potentially catastrophic failure of the reversed cell. Cell reversal in batteries has implications in terms of safety, as series arrangements of batteries are used in many applications. Typically series connected batteries are found in electric vehicles, solar and small-scale wind power installations, emergency power supplies and data centre uninterruptible power supplies (UPS) [19], occurrences of cell reversals in these installations are, as mentioned above, potentially catastrophic. It therefore suggested that the pH ‘disturbance’, observed in these discharge tests could be used as an indication of impending reversal of a cell within a string of series connected cells.

3. Discussion of the test results.

The results obtained from the discharge tests carried out on single cell Plantè and six cell SLI batteries will now be discussed.

During the experimental work a phenomenon was discovered and is characterised as follows:

1. The occurrence of a disturbance, at a point below the normal operating voltage range, in the measured value of the pH of the sulphuric acid electrolyte.
2. The magnitude of the pH disturbance increased as the discharge current increased.

The effect was apparent in the discharge tests but not during charging of the batteries. It is proposed that there are similarities in the results of the authors ‘experimental work with the results from Garche [20], the measurement of cell condition used by Garche being based on gas flow for the ‘aged’ cell and electrolyte concentration for the ‘new’ cell, whereas this work uses pH as the main indicator of cell condition for both ‘new’ and ‘aged’ cells.

3.1 Explanation of the pH disturbance in a ‘new’ cell

It was noted during the experimental work that when the battery was new the pH disturbance was characterised by a reduction in pH followed by an increase as shown by a discharge test carried out using ‘new’ Plantè cell as shown in figure 6.

Figure 6: Discharge characteristic of a ‘new’ Plantè cell, showing cell voltage (Volts) and electrolyte pH with pH disturbance.

Work carried out using a new battery by Garche [12] and Pavlov [21], reported that the positive electrode is considered to be limiting the battery capacity when the cell is new. The influence of the electrolyte concentration is important in a battery, and it has been established experimentally that the electrochemical activity of the $PbO_2/PbSO_4$ electrode depends on the concentration of the HSO_4^- bisulphate ions in the electrolyte solution of a lead-acid cell [13]. As the cell discharges the concentration of the electrolyte decreases and the performance of the positive electrode deteriorates as the acid concentration enters what Pavlov [13] refers to as the “passive low concentration region” where the concentration of HSO_4^- ions in the solution decreases at the expense of the formation of SO_4^{2-} ions. Furthermore the activity of the Lead-dioxide of the positive electrode decreases due to changes in the morphology of the Lead dioxide as the electrolyte concentration decreases below 0.5 M [2].

The condition of the cell at **point 1** on figure 6 is within the region referred to by Pavlov et al as the “Passive low concentration region”, where the bulk electrolyte concentration is below 0.5 M and the morphology of the lead dioxide (PbO_2) is α- PbO_2, which is the less active form of the two forms of PbO_2. According to Garche [12] during cell discharge the main reaction at the positive electrode is during discharge given by equation 6:

$$2PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4\left[PbO_2\right] + 2H_2O \qquad (6)$$

During the discharge the formation of lead sulphate $PbSO_4$ will block further discharge of PbO_2, and the remaining PbO_2 [PbO_2] will be electrochemically inactive i.e. $PbSO_4$ [PbO_2] lead sulphate and inactive lead dioxide is formed and the potential will fall [12].

Note: [ ] = inactive for example PbO_2 [PbO_2] indicates that not all of the lead dioxide is converted to lead sulphate, with some of the lead dioxide remaining unconverted.

Therefore, as the electrolyte concentration falls below 0.5 M, with a corresponding decrease in pH, the positive electrode becomes effectively passive. Another factor which has to be taken into account at this point is the possible reduction of oxygen at voltages below 1.23 volts as given in equation 7.

$$O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O \tag{7}$$

The effect of equation 7 will further reduce the concentration of hydrogen ions, and therefore causes the electrolyte pH to increase, i.e. become an increasingly positive value of pH; this is **<u>point 2</u>** in figure 6. At this point in the discharge test 13.98 Amp-hours of capacity had been discharged, the rated capacity of the Plantè cell being 15 Amp-hours. The negative electrode potential at this point decreases and lead sulphate on the negative (lead) electrode may be oxidised, according to Garche [12], as shown in equation 8 where lead sulphate is broken down as the negative electrode potential decreases.

$$PbSO_4\left[Pb\right] + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^- + \left[Pb\right] \tag{8}$$

Giving an increase in H^+ ions, which is detected by the pH meter as an decreasing pH of the electrolyte i.e. a more negative pH, this effect will increase as the reverse potential of the negative electrode increases, further decreasing the pH, at this point in the discharge, **<u>point 3</u>** in figure 6, here the cell voltage has declined to less than 1 volt and shortly thereafter the load is disconnected, the cell voltage recovers following the disconnection of the load.

3.2 Explanation of the pH disturbance in an 'aged' cell

The pH disturbance characteristic of an 'aged' cell was found typically to be as shown in figure 7. Comparing the 'new' and 'aged' batteries, it can be seen that the average value of pH is higher in the aged cell, reflecting deterioration in the condition and capacity of the cell.

Figure 7: Discharge test of an aged Plantè cell, showing cell voltage (Volts) and electrolyte pH with pH disturbance.

The pH disturbance of the aged cell is the inverse of the characteristic of the new cell of Figure 6, being characterised by a decrease in pH (point 1) to a minimal pH value (point 2) and subsequently an increasing pH (point 3). Figure 8 shows a similar test to that of figure 7, in this test the half-cell potentials were measured, and it can be seen from inspection that the negative half-cell potential peaks at a maximum value at approximately 650 seconds in the discharge test, the pH disturbance reaching the maximum value of pH shortly after this at approximately 670 seconds in the discharge test. Also at about this point in the test (650 seconds) the overall cell potential goes through a point of inflexion as the rate of decrease of the potential slows, with the potential of the negative electrode starting to increase in the negative sense, however, the positive electrode potential continues to decrease at an increasing rate, going through a point of inflexion at around 620 seconds in the discharge. It can be seen therefore as the negative electrode approaches reversal a pH disturbance occurs indicating on increase in the concentration of hydrogen ions in the electrolyte. Figure 8 has been included to show the positive and negative electrode potentials during a discharge test, it should be pointed out that the test relating to figure 7 was carried out at a discharge current of 6 amps, while the test shown in figure 8 was at a discharge current of 20 amps, hence the shorter discharge time of the test shown in figure 8.

Figure 8: Discharge test of an aged Plantè cell, showing overall cell voltage (Volts), half-cell potentials (Volts) and electrolyte pH with pH disturbance.

During discharge the reaction at the negative electrode as presented by Garche [12] is given by equation 9:

$$2Pb + SO_4^{2-} \rightarrow PbSO_4\left[Pb\right] + 2e^- \qquad (9)$$

Equation 9 shows the formation of the lead sulphate which will eventually blocks further reaction of the active Lead, Pb, on the electrode and any remaining lead [Pb] will be rendered electrochemically inactive, i.e., lead sulphate is formed and residual inactive lead remains, expressed as $PbSO_4\left[Pb\right]$. In figure 7 at about 1300 seconds the pH increases, the molar concentration of the bulk electrolyte decreases with an increasing pH; this corresponds to **point 1** in figure 7.

Figure 9 shows the over-discharge test carried out by Garche [12] on battery “a” which is an ‘aged’ cell. Due to the loading arrangement employed in this test the shift in potential is significantly higher with the reverse cell voltage approaching negative 2.5 volts, a discharge current of 2.5 amps compared to the 6 amps used in the Plantè cell discharge tests of figures

7 and 8 which did not undergo cell reversal during the discharge test. Inspection of figure 9 shows that this time it is the negative electrode which is the first to reverse polarity, as opposed to the new cell, referred to as battery "b" in the tests carried out by Garche [12], in the tests on battery 'b' the positive electrode reversed before the negative cell, and the positive electrode was found to be the limiting factor. Figure 9 shows the polarity of both electrodes reversing, resulting in cell reversal that is a similar test to the test carried out by the authors as shown in figure 5.

Figure 9: Battery 'a' cell voltage (aged) and corresponding cell electrode potentials during over-discharge [12].

Figure 10 shows the gas flow and oxygen content measured during the over-discharge test carried out by Garche [12], on the aged cell "a". It can be seen that there are two significant peaks in gas flow in the first half of the discharge test, these being the points at which the negative and positive electrode reverses polarity. In figure 10 the first peak occurs when the negative electrode goes into reverse polarity at approximately 4 hours in the test, followed at approximately 11 hours by the reversal of the positive electrode. As the tests carried out on the Plantè cell, with the exception of the cell reversal tests, were in isolation, reversal of both electrodes cannot occur.

Figure 10: gas flow and oxygen content of a single cell during over-discharge experiment [12].

As the polarity of the negative electrode [Pb] reverses the lead sulphate will be oxidised to lead oxide in the reverse reaction as lead sulphate layer is broken down, this reaction also resulting in hydrogen ions being formed as the water [H_2O] molecules are broken down as can be seen from the previous equation (8). Furthermore, oxygen evolution may occur (equation 10), depending on the potential at the beginning of over-discharge (at about 4.5 hours on Figures 9 and 10), or if all of the active material is oxidised to lead dioxide [12].

$$2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^- \qquad (10)$$

The resulting effect is an increase in the concentration of hydrogen ions as the negative cell reverses this corresponds to **point 2** on figure 7. At this point in the discharge test 3.42 Amp-hours capacity had been discharged, from the 15 Amp-hours rated capacity of the Plantè cell, compared to the 13.98 Amp-hours capacity which had similarly been discharged, during the test on a Plantè cell in a new condition. As the cell continues to discharge and the negative electrode now briefly takes a positive potential. Lead sulphate and inactive lead dioxide is formed and the cell potential will fall, as the electrolyte concentration falls with a corresponding decrease in pH, the positive electrode again becomes effectively passive, this corresponds to **point 3** on figure 7.

The discussion so far has concentrated on the pH disturbance in Plantè cells, however the same pH disturbance was observed during the discharge tests involving SLI batteries, with the pH disturbance for new and aged SLI batteries having the same characteristic as previously noted for the 'new' and 'aged' Plantè cells. In the test represented in Figure11 the electrolyte pH is being measured in one of the six cells in a 6 cell automotive Starting, Lighting and Ignition (SLI) battery.

Figure11: 6 cell SLI battery discharge test showing battery voltage, discharge current (Amps) and pH of one cell. Note the pH disturbance where the measured cell has reversed polarity.

It can be seen that a pH disturbance coincides with a potential step in the battery voltage discharge characteristic. The potential decreases and then slightly increases or recovers, where it is believed these recovery ‘overshoots’ are due to the high resistance of the lead sulphate and the onset of cracking of the sulphate layer [13]. The battery used in the test of Figure11 test had been in service for some and is hence referred to as aged and compares to battery “a” in the tests carried out by Garche [12] where one of the tests involved the over-discharge of a three cell battery. Moreover, figure 12 shows a discharge test on a six cell SLI battery where only one cell was being monitored for pH. However, it clear from figure 12 that there are in fact two ‘potential steps’, corresponding to two cell reversals. The cell being monitored with the pH sensor was in fact the first cell to reverse at 4500 seconds, and the reversal of the second and third cells can be clearly seen at 5500 and 6000 seconds respectively in figure 12.

Figure 12: SLI battery discharge test, showing batter voltage (Volts), discharge current (Amps). Note the three cell reversals, the first cell reversal also indicated by the cell electrolyte pH.

4 Conclusions

In summary the occurrence of a new pH ‘disturbance’ occurring during discharge of a lead-acid ‘wet cell’ battery, has been described and explanations for the difference in these pH disturbances between ‘new’ and ‘aged’ batteries have been proposed. Furthermore it has been demonstrated that this disturbance supports the published findings and theory proposed by Garche [12].

Reverse charging can occur in strings of cells, individual cells within the string may have lower capacities due to manufacturing deviations or due to accelerated ageing. In consequence the low capacity cell can be over-discharged which will result in reverse charging. [22]. A faulty or weak cell within a long string of cells under discharge could be driven into reversal resulting in the failed cell being effectively charged by the other healthier cells. The reversed cell could be subject to power dissipation of up to 5% of the entire battery power capacity, which can cause catastrophic failure [23]. If integral monitoring of the electrolyte pH were to be incorporated into individual cells, the pH disturbance would serve as an early and clear warning of impending cell reversal.

Possible applications include automotive electrical systems and battery cell monitoring.

Automotive electrical systems will progressively change during the next few years. Part of the automotive market will be taken over by so-called hybrid vehicles. The remainder of the automotive market will involve conventional vehicles with internal combustion engines, but with higher voltage electrical systems [24], however both types of vehicle will require batteries with multiple series connected cells. Another application is the monitoring of individual cells within a multi-cell battery systems of standby power and data centre Uninterruptible Power Supplies (UPS) [25].

This paper has concentrated on lead-acid cells, however, it is possible other types of cell may exhibit similar behaviour and could be monitored by measuring electrolyte properties such as pH. Therefore the monitoring of electrolyte pH should be viewed as an additional means of individual cell monitoring of series connected cells or batteries.

---

[1] A.G. Olabi. 100% sustainable energy. Energy 77 (2014) 1- 5.

[2] Wilberforce T, et al., Advances in stationary and portable fuel cell applications, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.02.057

[3] Alaswad et al. Developments in Fuel Cell Technologies in the Transport Sector. International Journal of Hydrogen Energy (2016), paper accepted. DOI: 10.1016/j.ijhydene.2016.03.164

[4] A.G. Olabi. State of the art on renewable and sustainable energy. Energy 61 (2013) 2- 5.

[5] Muhammed M. Vargonen. Modeling the impact of paste additives and pellet geometry on paste utilization within lead acid batteries during low rate discharges. Journal of Power Sources 273 (2015) 317- 323.

---

[6] Rotem Marom, Baruch Ziv, Anjan Banerjee, Beni Cahana, Shalom Luski, Doron Aurbach. Enhanced performance of starter lighting ignition type lead-acid batteries with carbon nanotubes as an additive to the active mass. Journal of Power Sources 296 (2015) 78-85.

[7] Crompton, T.,“Battery Reference Book”, Third Edition Newnes Books 2000, ISBN13: 978-0750646253, pp2/16.

[8] A.G. Olabi. Developments in sustainable energy and environmental protection. Simulation Modelling Practice and Theory 19 (2011) 1139–1142.

[9] Smith, G., “Storage Batteries”, Second Edition Pitman. ISBN 0 273 36087 6, pp5.

[10] The Centre for Low Carbon Futures 2012. Pathways for energy storage in the UK.

[11] Groves, P.D., “Electro-chemistry”, J Murray, 1974, ISBN 0 7125 2935 2

[12] Kiehne, H.A.,”Battery Technology Handbook”, Marcel Dekker Inc 2003, ISBN 0-8247-4249-4, pp50.

[13] Berndt, D., “Maintenance –Free Batteries A Handbook of Battery Technology”, Second edition, Research Studies Press, ISBN 0 86380 198, pp8.

[14] Crompton, T.,“Battery Reference Book”, Third Edition,Newnes Books 2000, ISBN13: 978-0750646253, pp1/16.

[15] Hamman.C.A.,Hamnett. A, Vielstich.W, “Electrochemistry”, Second Edition, Wiley, 2007, ISBN 978-3-527-31069, pp146.

---

[16] Vincent,C.A., Scotsati.B.,“Modern Batteries. An introduction to Electrochemical Power Sources”, Butterworth Heinemann ISBN 0-340-66278-6,1997, pp25.

[17] Bayuomy, M., El-Hefnaw,S,Mahgoub, El-Tobshy, A. 1994.“New techniques for battery charger and SOC estimation in photovoltaic hybrid power systems”. Solar Energy Materials and Solar Cells, 35, 504-514, ISSN 0927-0248

[18] Chetan.S, “Solar Photovoltaics, Fundamentals, Technologies and Applications”, Asoke.K.Ghosh ISBN 978-81-203-3760-2.

[19] Luque, A.,Hegedus, S.,“Handbook of Photovoltaic Science and Engineering”. Wiley. 2003 ISBN 13:978-0-471-49196-5(H/B), pp827.

[20] Garche,J., Jossen.A., Doring.H., 1997. “The influence of different operating conditions, especially over-discharge, on the lifetime and performance of lead/acid batteries in photovoltaic systems”. Journal of Power Sources., 67, pp201-212.

[21] Pavlov, D., B.Monahov, , 2004.“The influence of H_2SO_4 concentration on the mechanism of the processes and the electrochemical activity of the $Pb/PbO_2/PbSO_4$ electrcode”.Journal of Power Sources. 137, 288-308.

[22] Jossen,A, Garche. J, Sauer.D.U, 2004. “Operation conditions of batteries in PV applications”. Solar Energy. 76, 759-769.

[23] Perone, S.P, 1993. “Modeling the occurrences of cell reversals”.Journal of Power Sources, 41, pp277-290.

Table 1: Sulphuric acid properties [25].

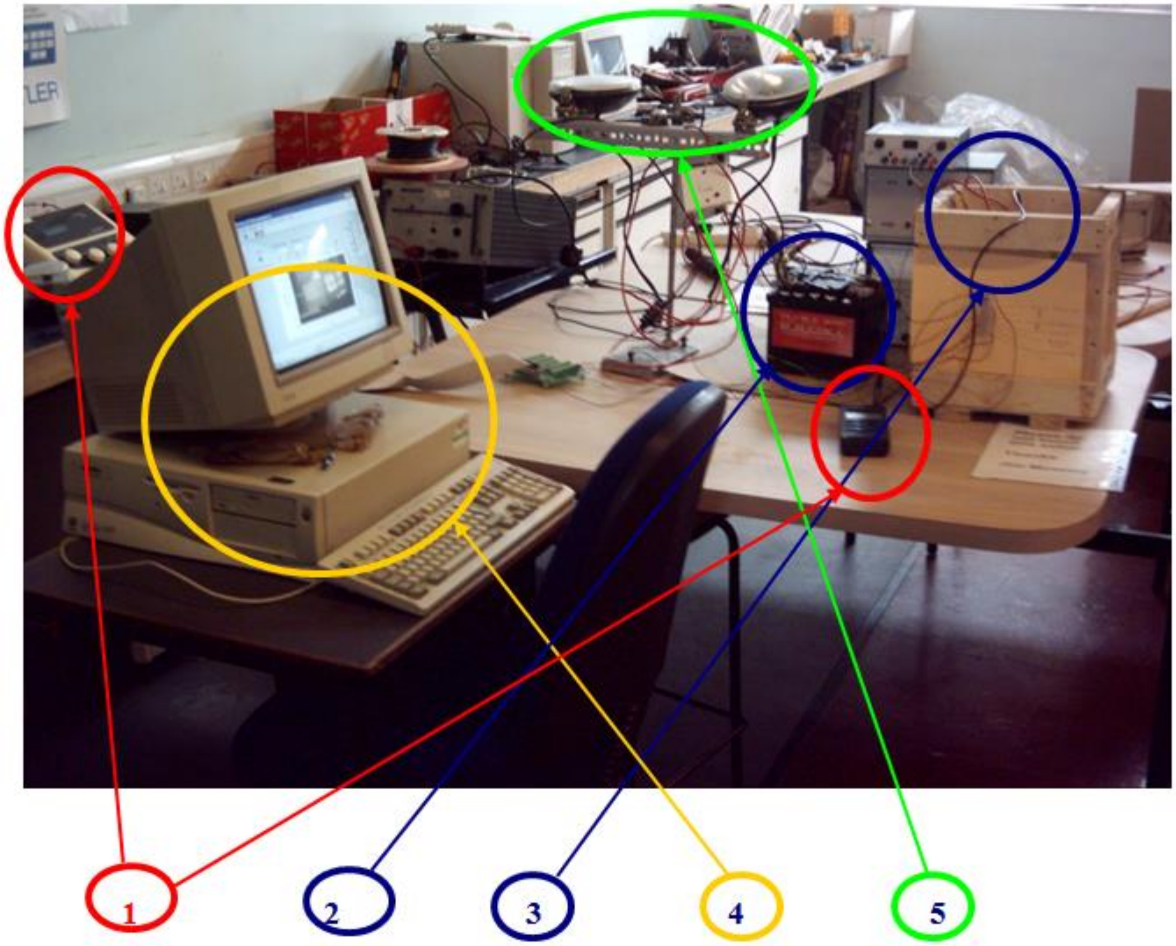
Sulphuric Acid Properties			
Content	Specific	Electrochemical	Cell Voltage

---

[24] Micka.,K. , 2004. “Contemporary trends in research and development of Lead-Acid batteries”. Journal of Solid State Electrochemistry 8, pp932-933.

[25] McCluer, S,“Battery Technology for Data Centres and Network Rooms. Lead-Acid Battery Options”, White Paper #30, APC Schneider Electric.

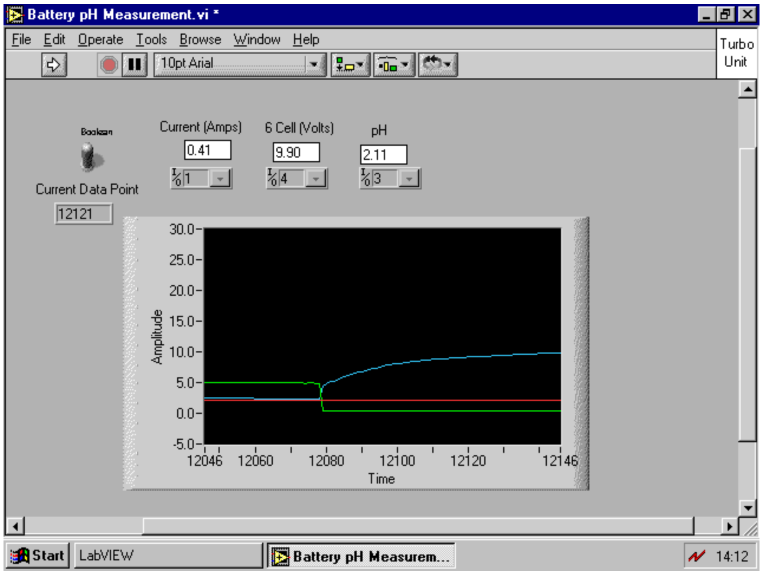
%wt	(20 deg C)	Amperehours/Litre	Volts
6	1.036	16.9	1.876
8	1.05	22.9	1.89
10	1.064	29.1	1.904
12	1.089	35.4	1.929
14	1.092	41.9	1.932
16	1.108	48.4	1.948
18	1.122	55.1	1.962
20	1.136	62	1.976
22	1.152	69.3	1.992
24	1.168	76.5	2.008
26	1.183	84	2.023
28	1.199	91.5	2.039
30	1.215	99.5	2.055
32	1.231	106.9	2.071
34	1.248	116.8	2.088
36	1.264	124	2.104
38	1.281	133	2.121
40	1.299	141.9	2.139



1. pH meters.
2. SLI battery.
3. Plantè cell inside protective wooden crate.
4. PC with LabVIEW© software for monitoring tests and recording data.
5. 12 V Lights used as load on SLI battery.

Figure 1: Battery testing facility.

Figure 2: Arrangement for locating pH sensor in Plantè cell.



Current (Amps) 0.41

6 Cell (Volts) 9.90

pH 2.11

Current Data Point 12121

Figure 3: LabVIEW© Front panel for pH monitoring.

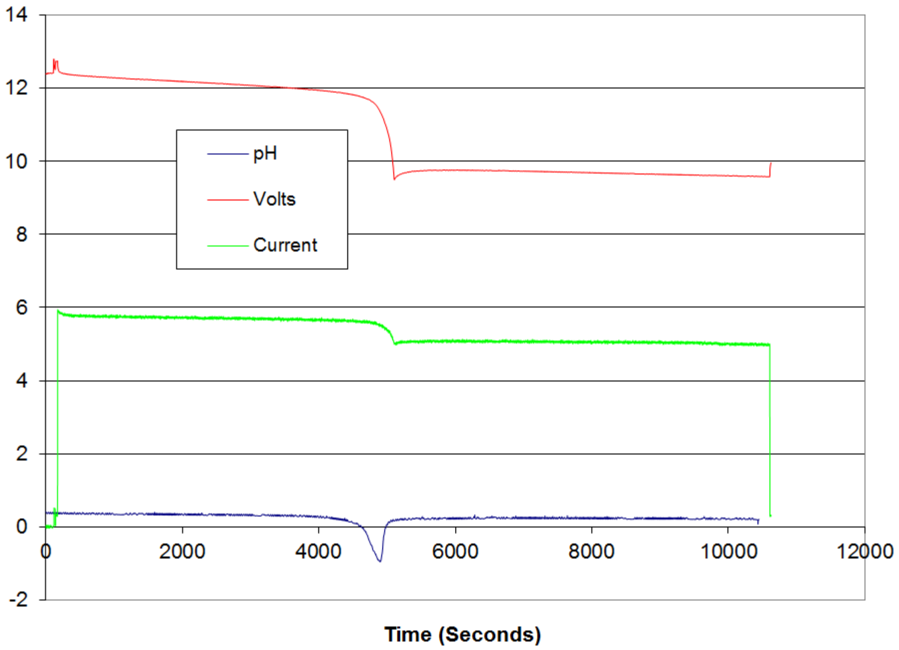


Figure 4: Discharge test on SLI battery, showing battery voltage (Volts), discharge current (Amps), and electrolyte pH.

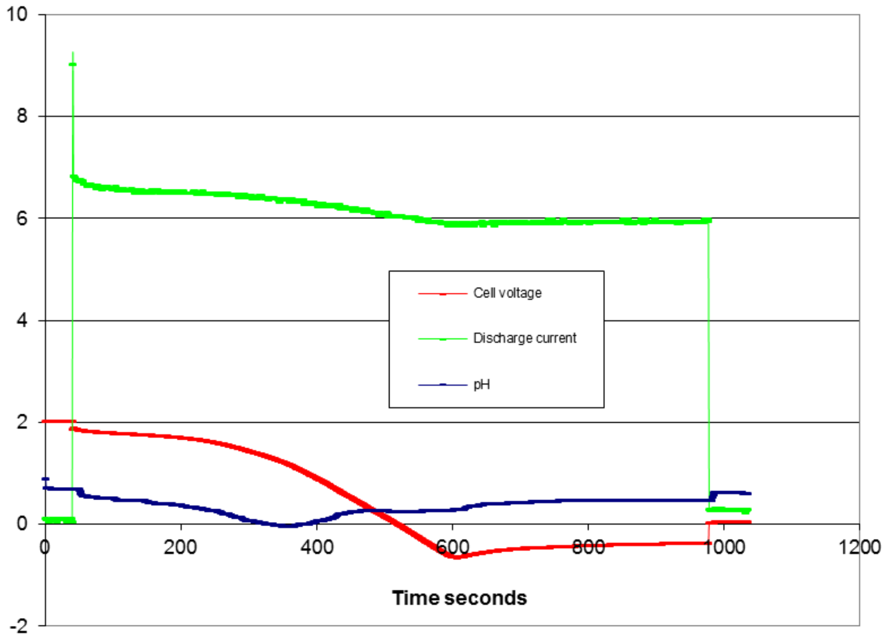


Figure 5: Plantè cell discharge test leading to cell reversal, showing cell voltage (Volts), discharge current (Amps) and cell electrolyte pH.

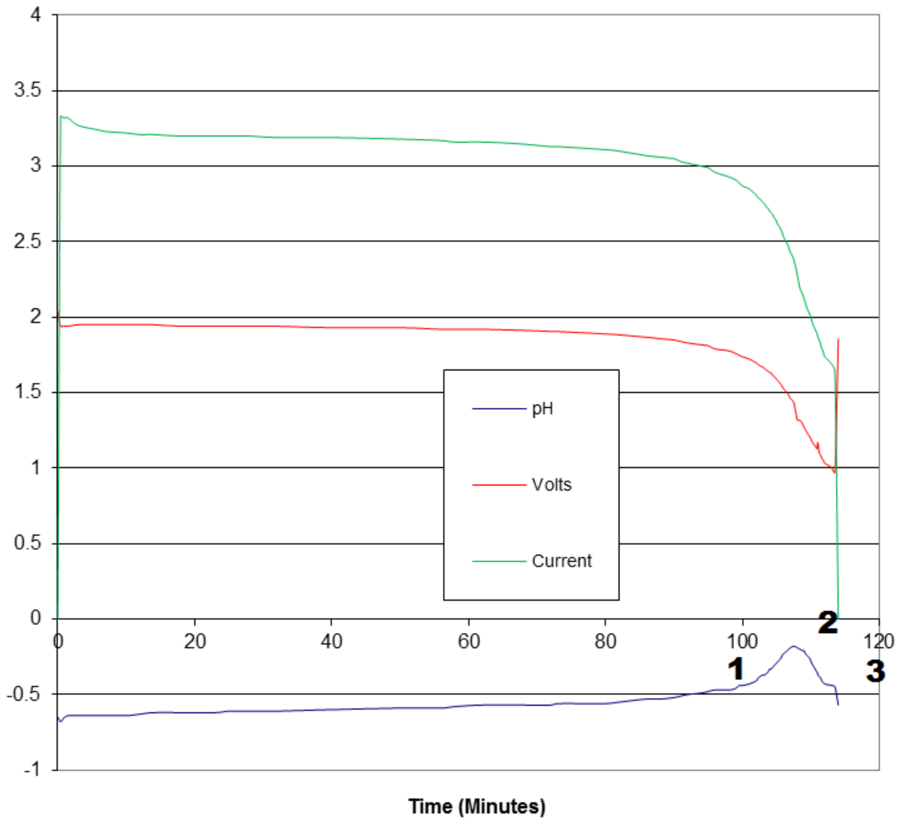


Figure 6: Discharge characteristic of a ‘new’ Plantè cell, showing cell voltage (Volts) and electrolyte pH with pH disturbance.

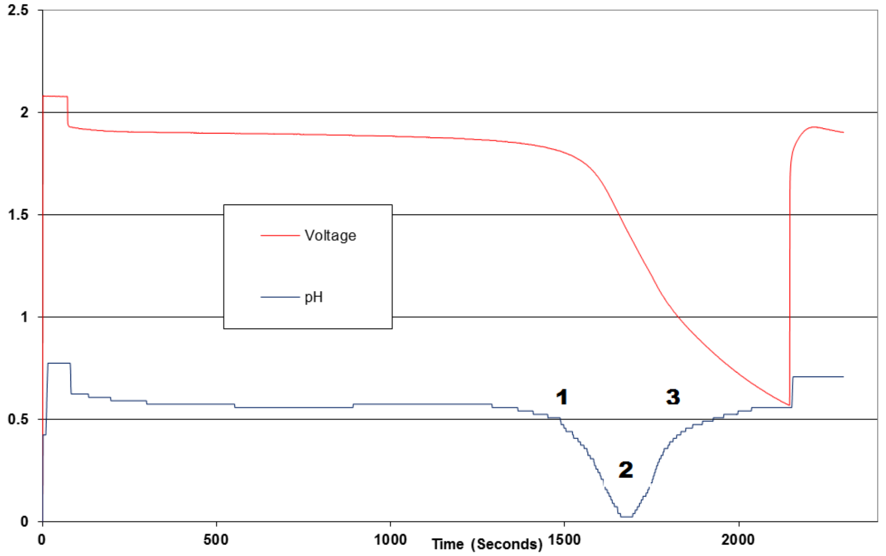


Figure 7: Discharge test of an aged Plantè cell, showing cell voltage (Volts) and electrolyte pH with pH disturbance.

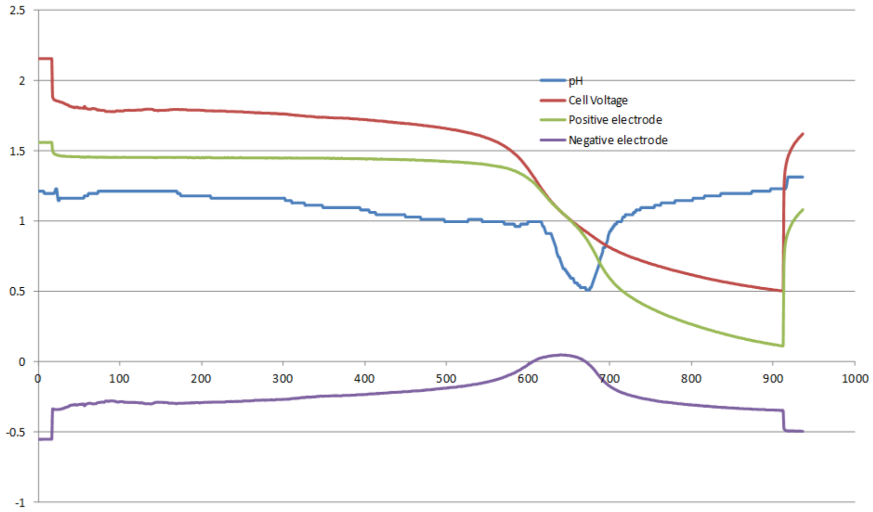


Figure 8: Discharge test of an aged Plantè cell, showing overall cell voltage (Volts), half-cell potentials (Volts) and electrolyte pH with pH disturbance.

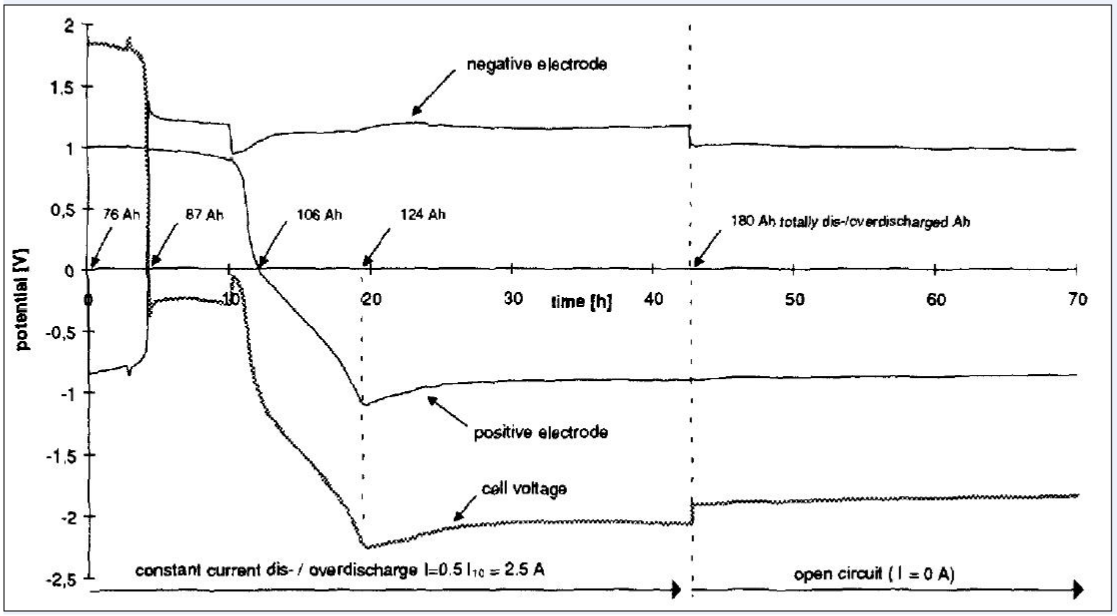


Figure 9: Battery 'a' cell voltage (aged) and corresponding cell electrode potentials during over-discharge [12].

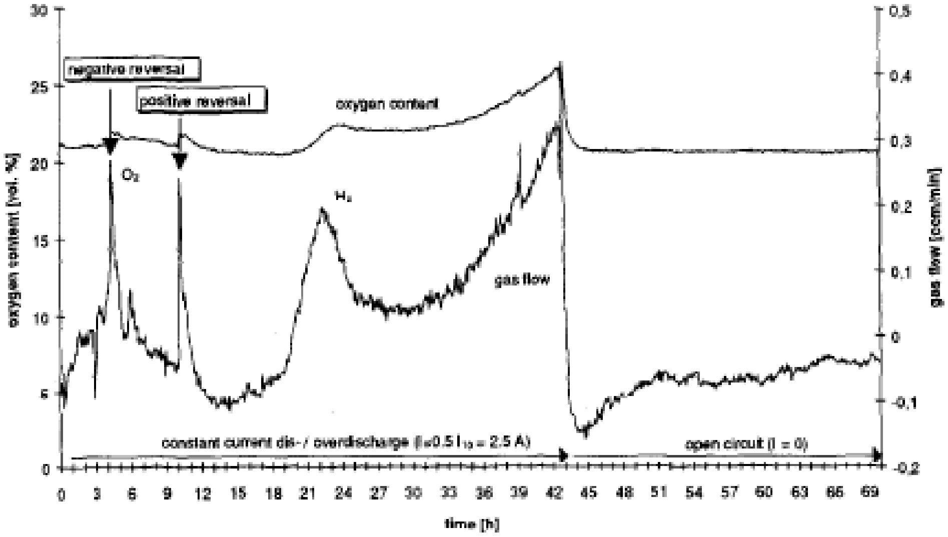


Figure 10: gas flow and oxygen content of a single cell during over-discharge experiment [12].

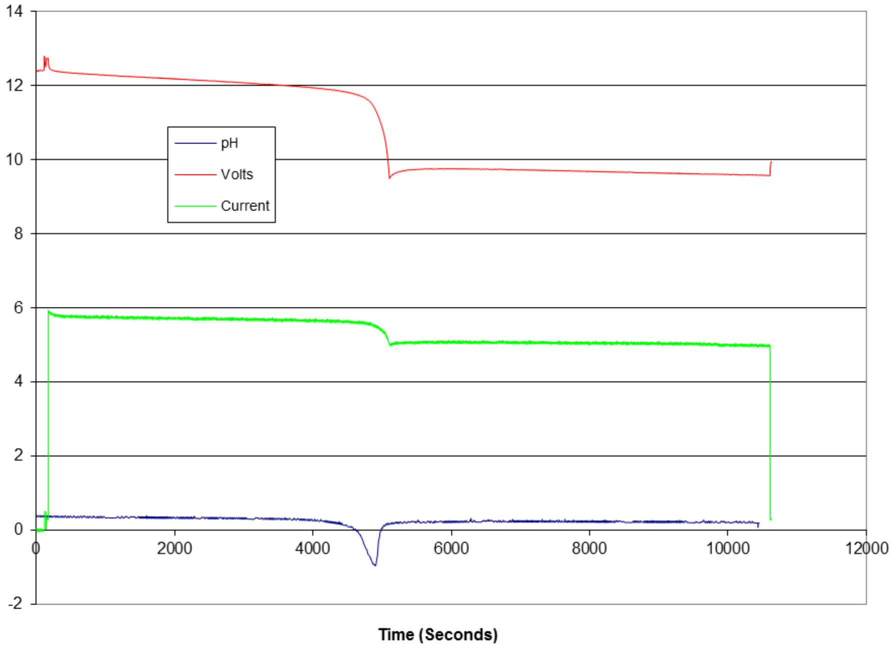


Figure11: 6 cell SLI battery discharge test showing battery voltage, discharge current (Amps) and pH of one cell. Note the pH disturbance where the measured cell has reversed polarity.

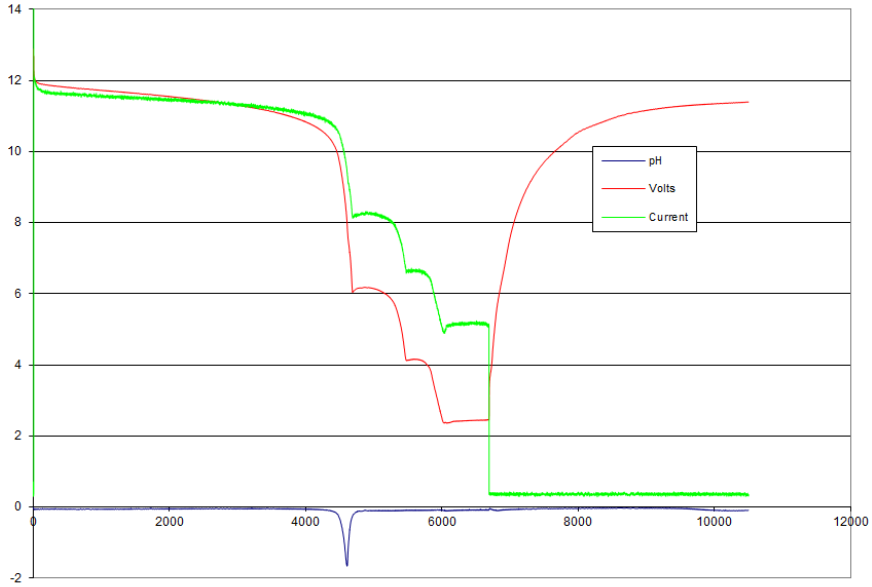


Figure 12: SLI battery discharge test, showing batter voltage (Volts), discharge current (Amps). Note the three cell reversals, the first cell reversal also indicated by the cell electrolyte pH.