Pulsing Lead-Acid Batteries

(Reversing 'hard' sulfation)

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Abstract

Various approaches to pulsing lead-acid batteries to drive 'hard' sulfation back into the reaction are reviewed, and the promising resistive based design is considered for accelerated desulfation

1 Introduction

Lead acid batteries have been with us for over 100 years now, and despite their heavy weight, they remain economical options for rechargeable (secondary) storage devices

Their chemistry is simple, with just over 2 volts generated per cell (gassing starts at 2.38 V), and reversible reaction given by:

NEGATIVE PLATE (Spongy lead) 0.356V:

$$\overbrace{\underbrace{\mathrm{Pb}}_{grey} + \mathrm{H_2SO_4}}^{discharging \Rightarrow} \Longleftrightarrow \overbrace{\underbrace{\mathbf{PbSO_4}}_{white} + 2\mathrm{e}^- + 2\mathrm{H}^+}^{\Leftarrow charging} \tag{1}$$

POSITIVE PLATE (Lead dioxide) 1.685V:

$$\overbrace{\underbrace{\mathrm{PbO_2}}_{brown} + \mathrm{H_2SO_4} + 2\mathrm{e}^- + 2\mathrm{H}^+}^{discharging \Rightarrow} \Longleftrightarrow \overbrace{\underbrace{\mathbf{PbSO_4}}_{white} + 2\mathrm{H_2}0}^{\Leftarrow charging} \tag{2}$$

The fact that one sees less sulfation on the positive than negative straps, is probably due to the water that accompanies lead sulfate production at the positive plates.

Such technology has several failure modes, but the predominant one tends to be sulfation, where given time (of the order of months), the lead sulfate crystallizes out into a 'hard' form (differing allotropes?). The sulfation actually progresses in stages, with the final level bonds being insulators, and it is this form that is being targeted here.

Given the quantity of lead employed in a battery, and the toxicity of lead to the environment (not to mention the sulfuric acid), a system that can extend the operational life of such batteries is highly desirable.

Many cures to restoring the reluctant sulfation back into the reaction have been suggested, but of the many trials, treating the battery with short electrical pulses has been confirmed successful, although the exact mode of operation is still up for debate.

This project is intended to run at a low budget, hobby level, with stock circuits being available in kit form for around $50. Commercial units exist at a comparable cost (`http://www.pulsetech.com/`), and the military has been taking advantage of such technology for over a decade now to ensure the readiness of its equipment in storage.

2 Which theory?

Some manner of theory would be most enlightening, for operating without one is like wandering in the dark, with too many things to try, and matters soon become very opinionated and loyalties to certain approaches develop.

It would seem that the insulator 'hard' crystals forms the dielectric of a capacitor, so in order to have current cross the lead sulfate, a high slew rate is suggested from the definition of capacitance, namely:

$$I = C\frac{dV}{dt} \tag{3}$$

where I is the current, C the capacitance, and V the voltage.

This would explain the success of the pulsing approach with its intrinsic high slew rate.

3 Variations on a theme

Having decided that pulsing is a good thing, still leaves the territory wide open to variations. Should the pulses be inductively or resistively produced; of what height, width and repetition rate?

Producing an inductive pulse is somewhat challenging, while a resistive pulse is simpler to implement. Two circuit kits exist for the inductor based, approach; the so called 'Couper' circuit (HomePower #77; June/July 2000), and the ‘Dutch’ variation (Elector #14; Sept. 2001). More recently a resistive pulse design has appeared (BA 80 and BLA 1000) in the form of a slow speed ‘German’ circuit from ELV (2003). Challenging is the fact that while the ‘Couper’ circuit is documented in English, the ‘Dutch’ circuit is in Dutch (though available in English) and the ‘German’ circuit is in German (translation available).

Due to the high currents and frequencies involved, a lot of the pulse can be lost over the connecting leads, so short sturdy wires are advised.

4 Standardization or Control

One dilemma is the inability to accurately gauge performance, as no form of standardization, or control, has been developed to compare against. This just fires the strength of opinions for various approaches.

One might anticipate the development of a standard cell in a beaker with the addition of aged lead sulfate crystals between the plates, to be driven back into the reaction by the pulser circuit.

5 Inductive Pulsers

The inductive approach typically operates impulses around 1 kHz, and can power itself from the very battery itself, loading up magnetic flux into a main inductor and then discharging this rapidly back across the battery.

How this achieves a high voltage pulse is seen directly from the equation for inductance:

$$V = L\frac{dI}{dt} \tag{4}$$

where V is the voltage, I the current and L the inductance. The ‘Dutch’ circuit may be taken as typical of the inductor approach.

The impulse is of very short duration and can be seen to have a ringing nature. The ringing frequency is a function of the circuit and not the battery as can be seen by trying the same experiment across a dummy load. A low resistance shunt shows that a 40 amp peak accompanies the main voltage peak. These high currents and high frequencies suggest the use of Litz wire for the connecting leads, since significant losses are noted in normal leads.

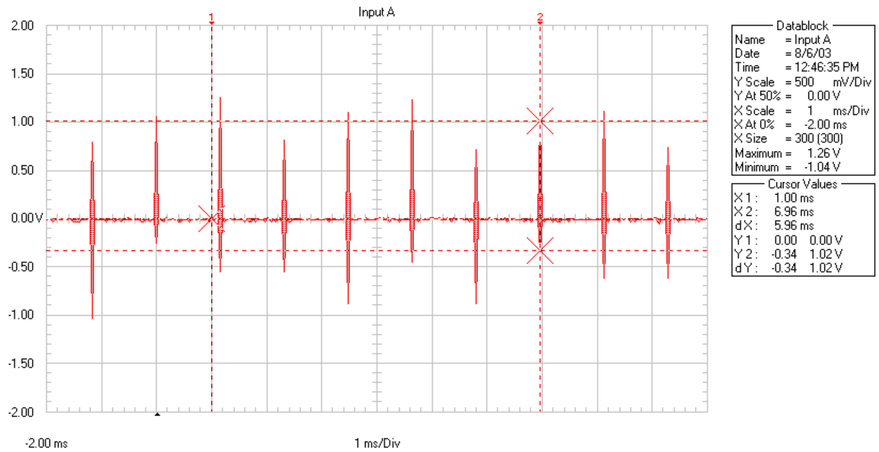

Fig 1: The main 'Dutch' 1 kHz impulse (with sampling artifacts)

The impulse seems very variable, but this is believed to be a sampling artifact of the digital oscilloscope being used.

The leading impulse is of very short duration and can be seen to have a ringing nature:

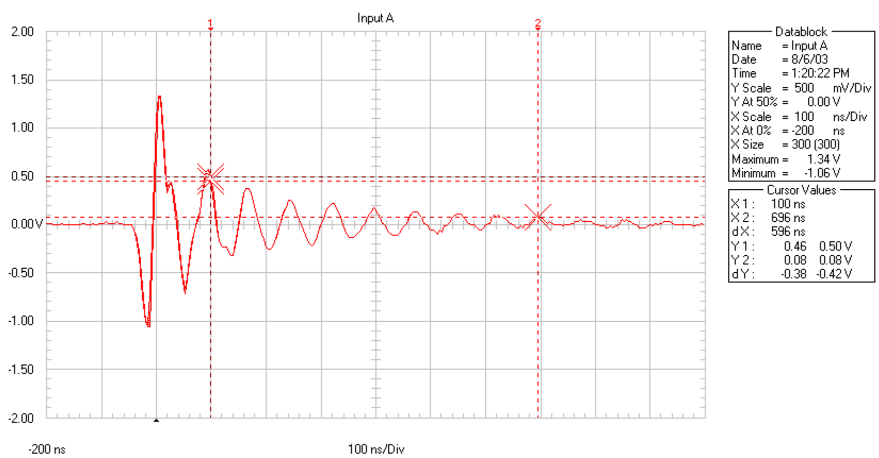

Fig 2: The leading impulse in detail

Note the negative nature of the leading edge.

6 The Need for Speed (breaking the 1 kHz limit by 1000 fold)

With present units, desulfation can take on the order of weeks to months, so there is a definite need for a highly accelerated version, if at all possible.

Attempting to increase the pulse rate limits the time available for the inductor to get up to energy in inductive based designs, and so is counterproductive in such cases.

Given all the resultant problems associated with inductive pulse circuits, it is anticipated that accelerated designs will be based upon the simpler resistive pulse approach, in which it is also easy to accommodate protection against accidental reverse connection.

6.1 Load based designs (a paradigm shift)

How a resistive based design achieves desulfation should become clear when looking at the inductive based plots (figure 2), for some actually hit the battery with a negative pulse.

The simplest approach to locate the optimal parameters is to use a pulse generator with abilities up to about 250 kHz to drive a power transistor across a power resistor.

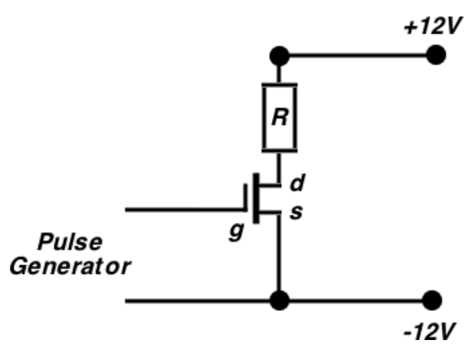

Fig 3: Resistive schematics

Building a circuit based on this new approach and 1 Ohm main resistor gave rise to the following wave forms:

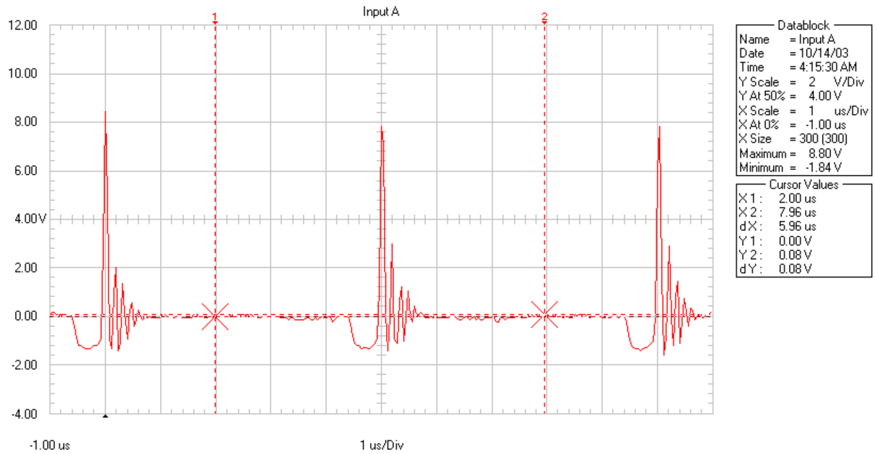

Fig 4: The main 'resistive' 200 kHz impulse (with sampling artifacts)

One needs to keep in mind that at these high frequencies (ringing is taking place at around 5 MHz) the inductance of most power resistors will make a significant contribution to its overall impedance.

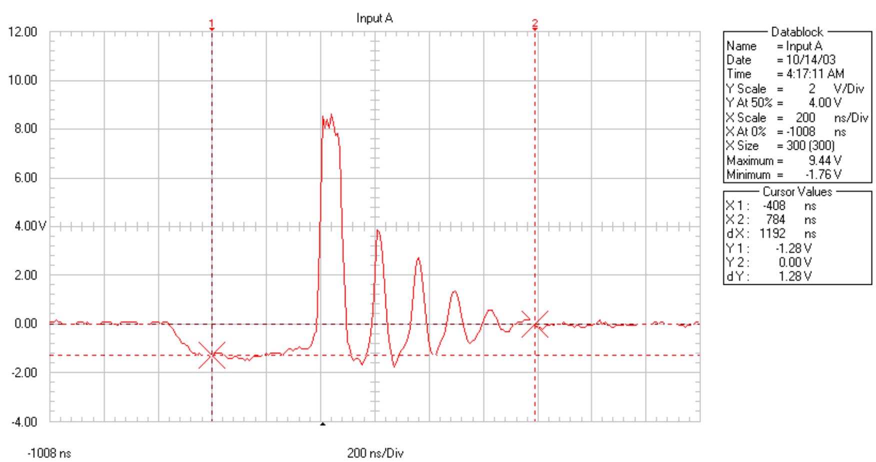

Fig 5: The impulse in detail for 200 kHz: 1 Ohm load

In practice it is found possible to go as high as 1 MHz for the pulse rate, which is a one thousand fold pulse rate improvement over the commonly used 1 kHz.

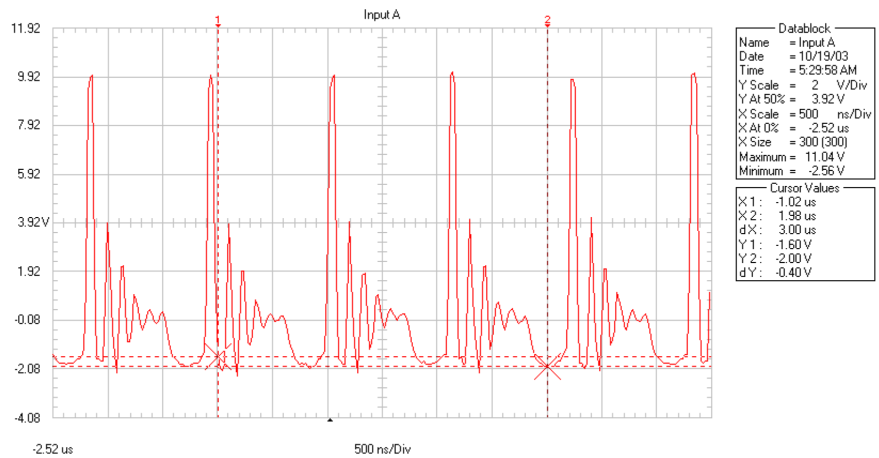

Fig 6: The impulse in detail for 1 MHz: 1 Ohm load

With observed slew rates up to 200 MV/s.

Increasing the load resistor to 10 Ohm only halves the bounce height:

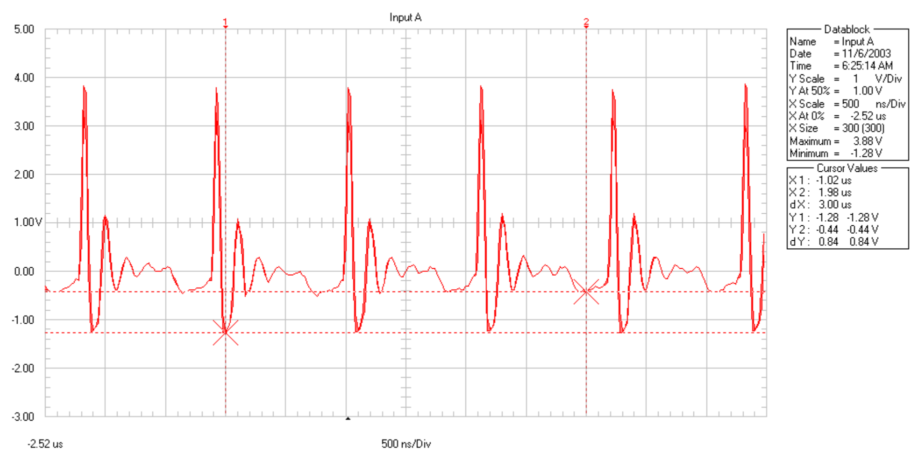

Fig 7: The impulse in detail for 1 MHz: 10 Ohm load

Relaxation times as high as 4μS have been seen in bad batteries, so 250 kHz might be a more realistic limit on the pulse rate.

The intriguing thing about the resistive approach is that the over-voltage pulse is being generated by the battery itself and not the circuit, and so avoids the problem about how to get the pulse into the battery.

At 1 MHz on a 1 Ohm circuit the power dissipation is excessive at 15 W, and a move to 10 Ohm sees the power dissipation significantly reduced to 3 W (most of it in the resistor), while the height of the over-voltage pulse is only halved. This may be a desirable change, given the gassing associated with high over-voltages.

6.2 Determining the optimal pulse width

Having achieved the maximal, and so optimal, pulse rate of 1 MHz, one can see that 300 nS is the optimal pulse width by extending the width duration, to yield:

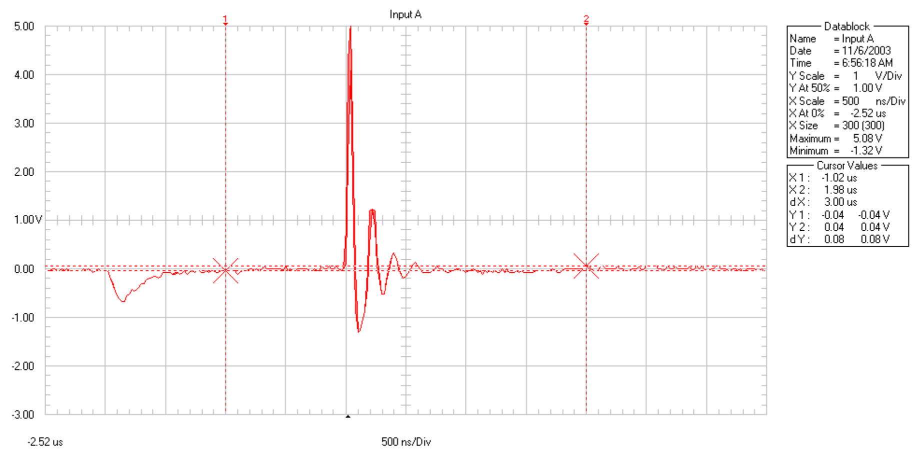

Fig 8: The impulse in detail for extended pulse width

from which it is clear that there is no benefit in pulsing longer than 300 nS.

So, of the three parameters to be optimized (pulse width, rate and bounce height), we have located parameters for the first two, namely 300 nS for the width, 1 MHz for the rate, and further, the bounce height should be limited to avoid gassing, namely should not rise above 14.28 V. Given that a fully charged battery rests at 12.68 V, this suggests arranging for a bounce height of about 1 V.

7 What still needs to be done

Naturally testing the performance of the accelerated load approach is first on the list of things to be done.

If accelerated performance is indeed noted, the design would benefit from detailed investigation of the effect of the pulse width, strength and rate. The over-voltage pulse will inevitably induce gassing, since too high a rate will overpower the mechanism of gas recombination. This may turn out to be a limiting factor in how fast one can desulfate in practice, most especially for sealed lead-acid batteries.

The circuit also needs the addition of protective diodes, a Zener to protect the transistor and a power diode to protect against reverse connection.

For the production circuit that may follow, the 200 kHz TL494 SMPS controller (less that $1 a piece) may be a suitable replacement for the 555 oscillator that was initially used for low speed circuits; or better still, the faster 74HC123 to achieve 1 MHz pulse rates.

8 Metering progress

Since sulfation locks away the electrolyte, the float voltage (via Kelvin contacts) might be a very good gauge of progress with regard to desulfation.

The electromotive force (EMF) is given by the Nernst equation:

$$\mathrm{EMF} = \mathrm{EMF}_0 - \frac{RT}{nF} \ln Q \tag{5}$$

where EMF_0 is 2.041 V and n is 2 for the lead acid cell, $F = 9.6485309 \times 10^4$ C/mol and $R = 8.314510$ J/(K mol), Q is the thermodynamic reaction quotient and T is the absolute temperature in Kelvin. The voltage is therefore a function of both temperature and electrolyte concentration and so may be used as an indirect measure of the electrolyte strength, with due caution being taken for the role of temperature.

Roughly speaking a 0.2 V recovery in open circuit voltage corresponds to about 25% of the capacity, with about 5 mV per degree centigrade above 25°C due to temperature. This makes for a non-intrusive method for monitoring progress.

On the other hand, the pulse height which reflects internal high frequency impedance might also make for a good gauge of progress. This may be preferable over monitoring the float voltage, which is not seen until after a significant rest period.

9 Ultra-low powered unit

Accelerated desulfation is all well and good, but prevention is much better than curing a battery that is nearing the end and struggling on that last little bit of unsulfated plate.

So the need for an ultra low powered, robust unit, may be of considerable more significance than an accelerated approach, although the later may be the best route to understanding the process of desulfation.

Even here the ultra-high frequency approach might have a significant role, since turning it to ultra-low power is as easy as increasing the value of the main discharge resistor.

10 Circuit Design

If one is powering from the battery itself, one is dealing with a self made dirty power source, so the pulser circuit needs to be strongly decoupled, via a resistor, and the smoothing needs to include two capacitors in parallel, an electrolytic for size, and a fast small capacitor to clip the pulses. One might also add a rectifying diode to cover the case where the battery source might be flattened momentarily by the pulse load. An inductor before the diode would avoid riding the pulse peaks which can in principle rise rather high.

One might also consider building one's own pulse generator based on NAND gates:

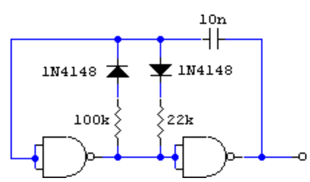

Fig 9: HomeBrew Pulse generator

A power diode could also be added to protect against reverse connection.

Other possible additions:

* A low voltage cut-off so the pulser could be permanently attached.
* Double leads to the battery terminals (Kelvin contacts), one set for the pulse itself, the other for monitoring pulse strength at the battery, as opposed to at the circuit.

11 Load Tests

With a battery load tester (100 amps for 10 secs) one can go about assessing the effectiveness of the resistive high rate pulser.

A candidate battery should first be charged to eliminate all soft sulfation. Then a load test can be performed before and after the application of a period of desulfation, the charge being maintained during pulsing.

It has been noted that for severely sulfated cases, the load voltage first drops under pulsing, and this might be accounted for if the lead sulfate goes through a less dense form before being electrolyzed.

Recovery ability is perhaps best characterized by the change in load voltage per day per Ah capacity.

11.1 Test results for an aged battery

12 Patents

Searching the US patents (`www.uspto.gov/patft/index.html`) shows that three classes of desulfator are being considered; the inductive and resistive as mentioned above, but also a capacitive approach where the capacitor is discharged across the battery. The capacitive approach will also suffer the same speed limitation as the inductive, again due to the time needed to charge up.

* Chiang (high pulse rate inductive/resistive)
  - 6,479,966 (2002)
  - 6,344,729 (2002)
* Gelbman (high pulse rate capacitive: BatteryMinder)
  - 6,184,650 (2001)
* Bynum
  - 0019257 (2001)
* King (high pulse rate)
  - 5,891,590 (1999)
* Gali (high pulse rate)
  - 35,643 (1997)
  - 5,633,575 (1997)
  - 5,592,068 (1996)
  - 5,084,664 (1992)
  - 5,063,341 (1991)
* Campagnuolo
  - 5,677,612 (1997)
* Phommarath
  - 5,525,892 (1996)
* Gregory
  - 5,491,399 (1996)

Reference Material

Lead Acid Desulfation discussion board (dedicated to the 'Couper' approach)
http://pub36.ezboard.com/bleadacidbatterydesulfation

* *Couper circuit*
http://www.homepower.com/files/desulfator.pdf

* *Dutch circuit*
http://www.elektor-electronics.co.uk/

* *German circuit*
http://www.elv.de/

* *Battery PaceMaker*
http://www.batterylifeplus.com/

* *RediPulse*
http://www.pulsetech.com/

* *BatteryMinder*
http://www.vdcelectronics.com/

DC converter basics
http://www.powerdesigners.com/InfoWeb/design_center/articles/DC-DC/converter.shtm