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High Efficiency lead acid battery formation

- *The lead acid battery formation process is highly inefficient. It accounts for approximately 50% of the total energy usage of battery manufacturers*
- *It also has additional costs of scrap and rework*
- *The present inefficiency increases the process time as well as the energy usage*
- *This presentation shows the R&D and field trials carried out by the collaborators. It demonstrates that an understanding of the chemistry can provide a more efficient process that will save LAB manufacturers hundreds of thousands of USD/annum.*

A report compiled by:

- UK Powertech Ltd
- Digatron Industrie-Elektronik GmbH
- Energy Storage Publishing Ltd
- Ecotech Energy Solutions Ltd

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The personnel and participating companies

- Mark Rigby – UK Powertech, Managing director and electrical connector engineer

- Mike McDonagh – Ecotech Energy Solutions and Energy Storage Publishing, Battery consultant and Bestmag technical editor

- Kevin Campbell – Digatron power electronics, Global Strategy and electronics engineer

Combined experience of over100 years in the battery industry.

Summary of 2 years R&D and field trials.

- UK Powertech, Digatron and ESPL have carried out 4 years of R&D, and engaged in field trials with 5 international battery manufacturers
- The first stage of the project was to remove the inefficiency of high resistance formation connections. This work led to a new connector design, formation rectifier cable modifications, and new maintenance procedures. All of which, drastically reduce process costs
- This measure alone gave manufacturers a minimum annual saving of between a ½ and 1 million USD in formation energy and scrap costs
- Further savings from a more efficient process in scrap, rework and formation time (higher output), will practically double this amount
- The current project examines the fundamental processes that convert the unformed plate active material into the charged PAM and NAM of the lead acid battery.
- A new charging methodology is proposed based on laboratory results and collaboration with LAB manufacturers

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Results of field connector trials

All costs are in USD normalised to 5 million batteries per annum

Formation input is 5 times the Ah capacity, charging voltage is 16.5V/battery

Average manufacturing cost per battery is 21 USD

Energy cost is 0.18 USD/kWh

5% saving = 17.5 x 75 x 5 x 5,000,000 x 0.05 x 0.18 = 295,313 USD

Factory	Energy saving	Incidence of arcing damage	Scrap saving from arcing	Rework saving from arcing	Confirmed cost saving	Potential total cost savings
F1	281,250	None	405,000	250,000	281,250 (energy)	**935,250**
F2	180,984(3.25%)	None	405,000	250,000	180,984 (energy)	**835,984**
F3	Not monitored	None	270,000	275,000	545,000 (arcing)	**840,313**
F4	Not monitored	4 in 180	396,000	244,500	508,500 (arcing)	**803,813**
F5	Not monitored	2 in 180	400,545	247,250	514,280 (arcing)	**809,593**

High resistance formation circuit – effect on efficiency of current absorption and level of voltage response

High Efficiency lead acid battery formation

Voltage is set to a value of 16.5 V

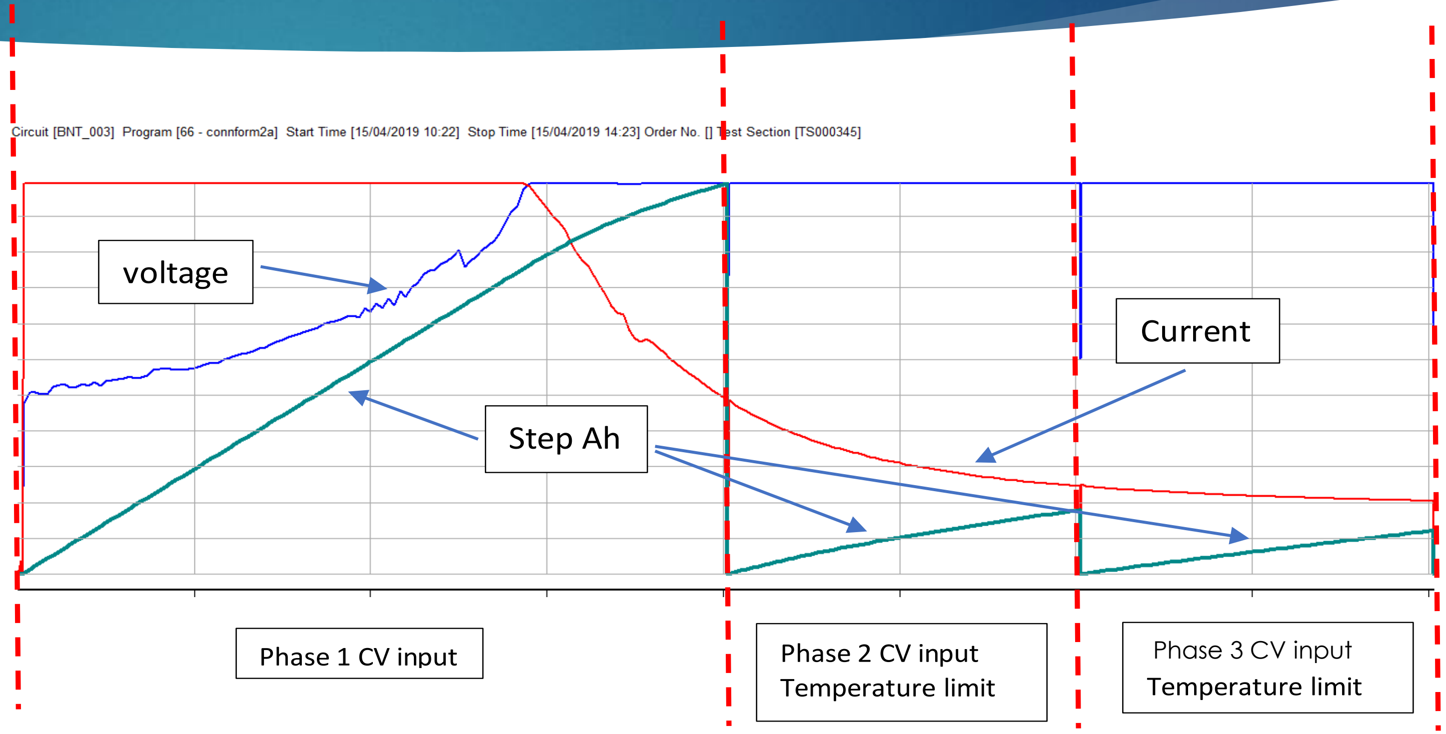
Current is constant until voltage limit is reached

Current declines as the battery becomes more charged

The time to reach the voltage limit determines the Ah input during the maximum current draw.

A high resistance connection will have a steeper voltage rise and fewer Ah input due to the current decline.

This means more Wh (higher energy consumption and fewer Ah



Low resistance formation circuit, effect on efficiency of current absorption and level of voltage response

High Efficiency lead acid battery formation

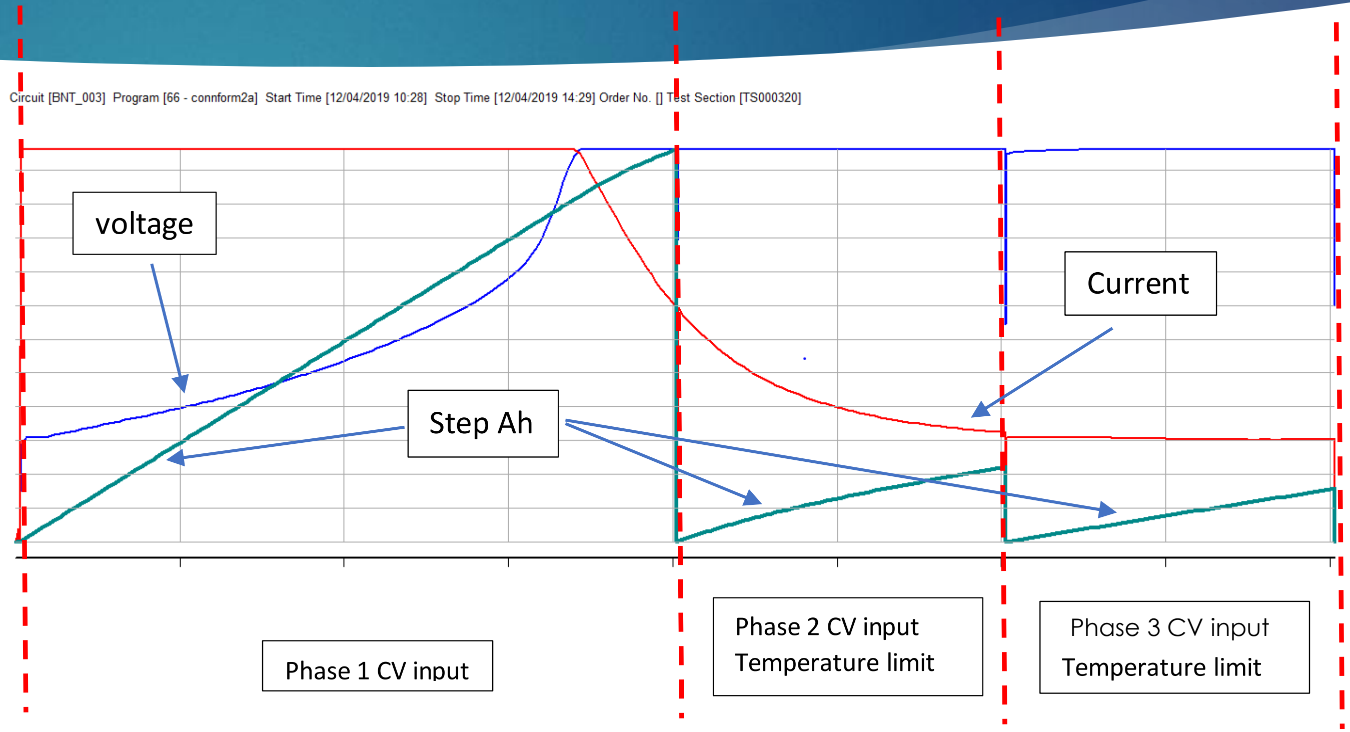
Voltage is set to a value of 16.5 V

Current is constant until voltage limit is reached

Current declines as the battery becomes more charged

The time to reach the voltage limit determines the Ah input

The longer it takes to reach the voltage limit the lower the voltage during the Ah input.



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Purpose of battery formation

First time the active materials are formed into the positive and negative plates.

Very low efficiency around 4 - 7 times the Ah capacity is required to completely convert the green active mass into the formed active mass.

The formation reactions can be simplified to:

Positive: $PbSO_4 + H_2O = PbO_2, + H_2SO_4 + 2e^- + 2H^+$

Negative: $PbSO_4 + 2e^- + 2H^+ = Pb + H_2SO_4$

The general overall reaction:

$$2\,PbSO_4 + 2\,H_2O = PbO_2 + Pb + H_2SO_4 \quad \text{(reversible)}$$

It is important to note that sulphuric acid is a by-product which increases in concentration as the formation reaction proceeds.

Acid soaking – the starting point for the chemistry of active material formation

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According to Detchko Pavlov the following reactions occur during the soaking process:

$$4PbO + SO_4^{2-} + H^+ = 3PbO.PbSO_4.H_2O \quad \ldots\ldots\ldots1$$

$$3PbO.PbSO_4.H_2O + SO_4^{2-} + H^+ = 2(PbO.PbSO_4) + 2H_2O \quad \ldots\ldots\ldots2$$

$$PbO.PbSO_4 + SO_4^{2-} + 2H^+ = 2PbSO_4 + H_2O \quad \ldots\ldots\ldots3$$

$$4PbO.PbSO_4 + 4SO_4^{2-} + 8H^+ = 5PbSO_4 + 4H_2O \quad \ldots\ldots\ldots4$$

All of the above reactions result in alkali conditions with a pH dependent upon the activity of the SO_4^{2-} ion.

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From the previous slide, the compounds formed are a variety of sulphates including basic sulphates of the form:

$xPbO.\ PbSO_4.H_2O$

This is a different starting point when compared to battery recharging in service

Most of the lead compounds in the active mass after soaking are the divalent form. The application of an electric current removes 2 electrons from the positive, giving the tetravalent ion.

The two removed electrons are transferred to the negative plate to fill the electron vacancies in the negative plate divalent lead ions.

i.e. PbO_2 is formed in the positive and Pb at the negative

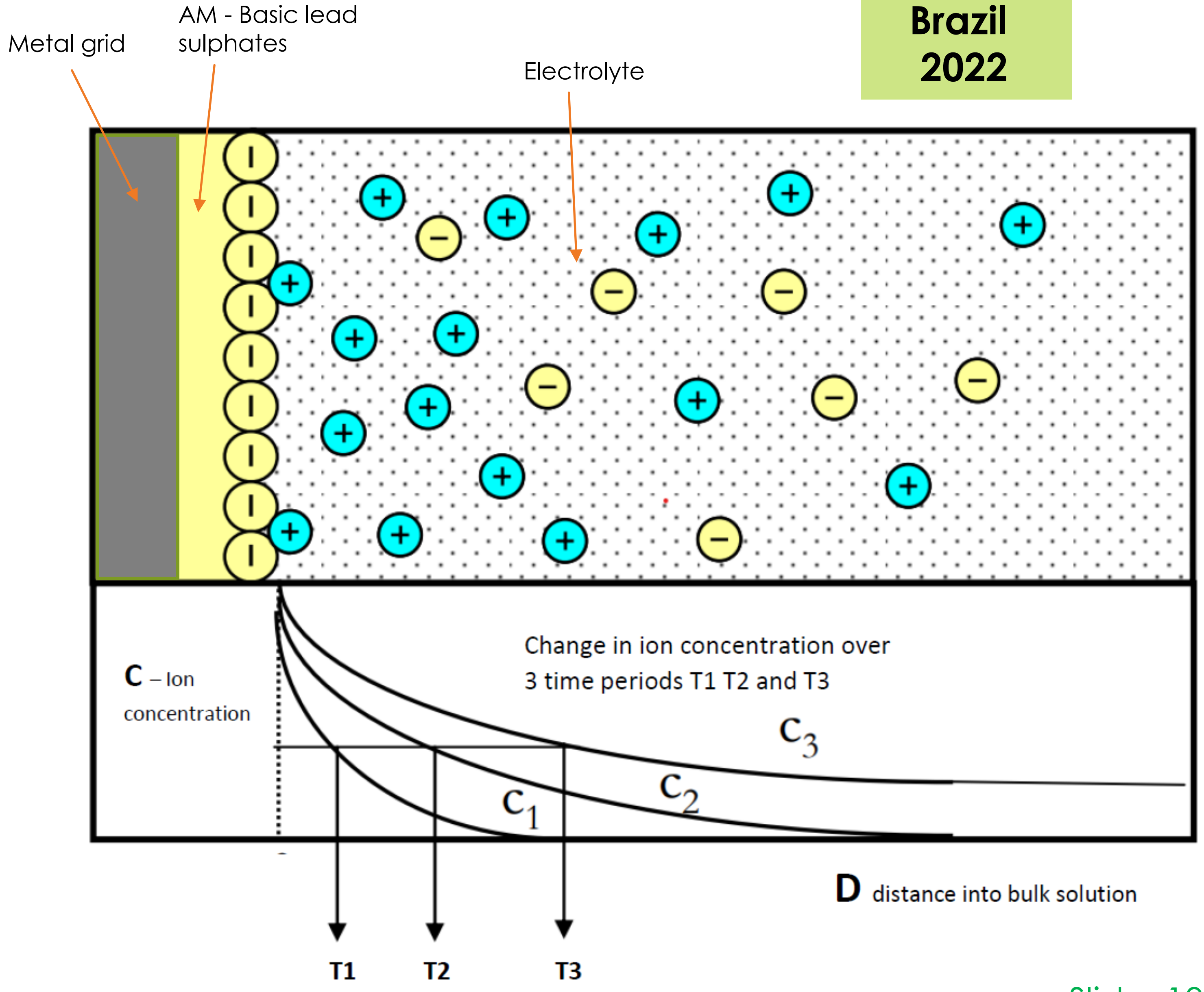
Pb^{2+}	$- 2e^-$	=	Pb^{4+}
Lead (sulphates, monoxide etc)	$- 2e^-$	=	Lead dioxide
Pb^{2+}	$+ 2e^-$	=	Pb
Lead (sulphates, monoxide etc)	$+ 2e^-$	=	Pure lead

High Efficiency lead acid battery formation

Ion polarisation on battery electrode.

As formation progresses the concentration of sulphate ions in the electrolyte increases.

This raises the total voltage of the electrolytic cell and increases the energy required for the conversion of $PbSO_4$ to Pb and PbO



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Origin of battery resistance and composition of on-charge voltage

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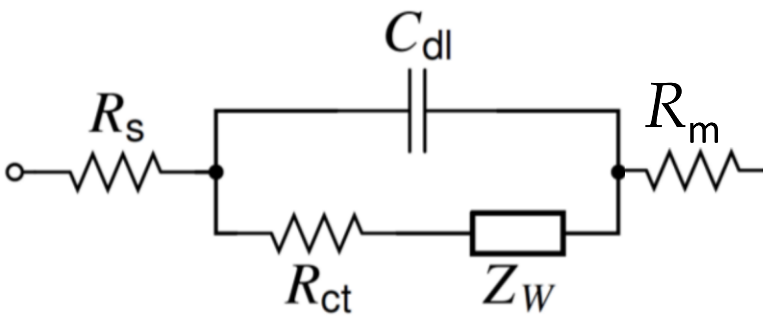
- The resistance of the circuit is comprised of metallic and reactive components.



Total resistance = $R_s + R_{ct} + Z_w + C_{dl} + R_m + Z_W$ (Warburg element) = $A_W/(j\omega)^{0.5}$
R_s is the electrolyte resistance

C_{dl} is the double-layer capacitance at the electrode/electrolyte interface

R_{ct} is the faradaic (charge transfer) resistance at the electrode/electrolyte interface, and

Z_w is the Warburg impedance

When an AC signal $I = I_0 \sin(\omega t)$ is applied to the cell under study, the response is given by $V = V_0 \sin(\omega t - \varphi)$, where I_0 and V_0 are signal amplitude, ω = 2πf (f is frequency, Hz), and ϕ is the phase angle.

- Voltage = current x resistance, V= I x ($R_s + R_{ct} + Z_w + R_m + C_{dl}$)
- The relative contribution of each of these components to the battery voltage will change with time during the formation process. The metallic components will alter very little but the reactive elements of Cdl and Zw are related to the electrolyte density and the ion concentration at the double layer/plate interface on charge

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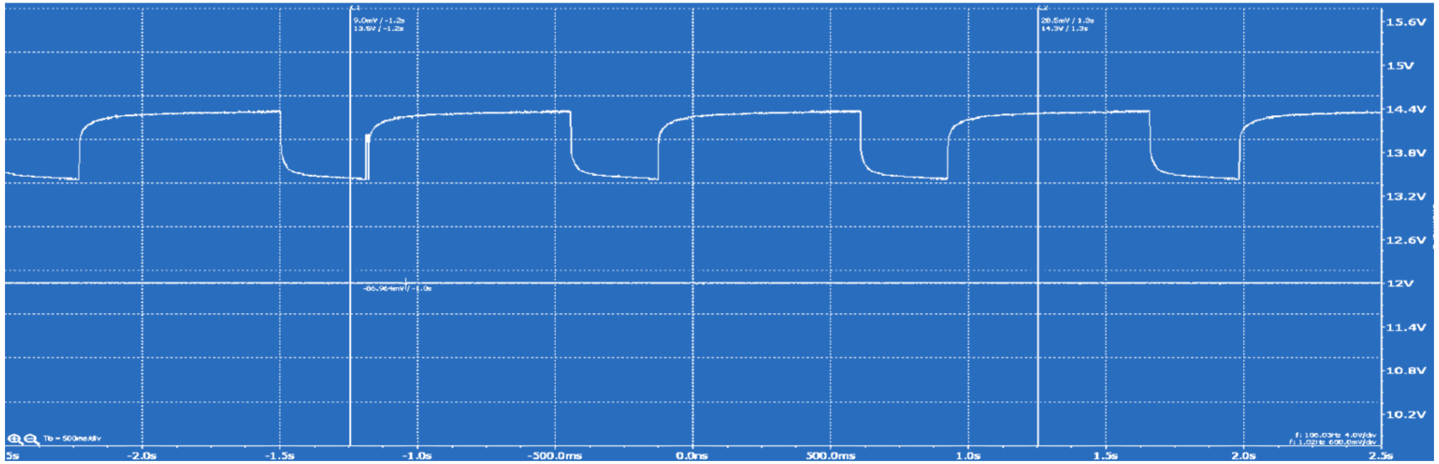
High Efficiency lead acid battery formation

Determining the SOC during formation

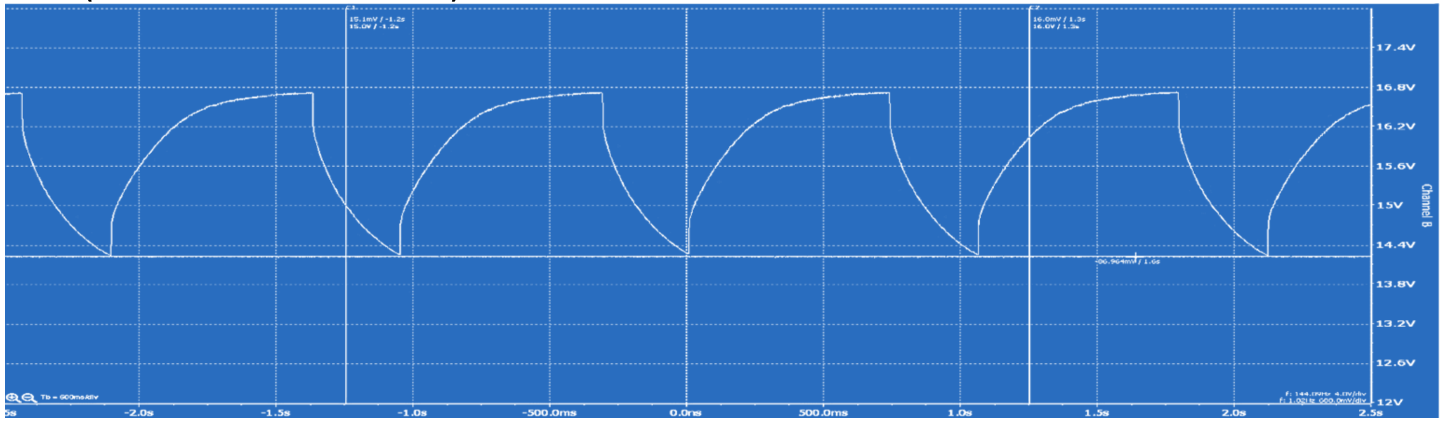
Battery voltage response to a single constant current pulse at different stages into the formation process

The contribution of the different components of the Randle model to the total voltage is clearly shown in these two measurements

30 mins into programme
(700ms on 300ms off)



3 hours into programme
(700ms on 300ms off)



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The lab trials conducted at UK Powertech with Digatron test equipment

Test area water bath with Digatron take-off leads.
4 ccts: charge/discharge, 32V 100A
Measurements:
Current
Voltage
Temperature
Time

Digatron control computer :
4 ccts
Multi functional controls
Monitoring and control of all battery parameters including:
Ah, Wh, Temp, charging algorithms, pulsing etc.

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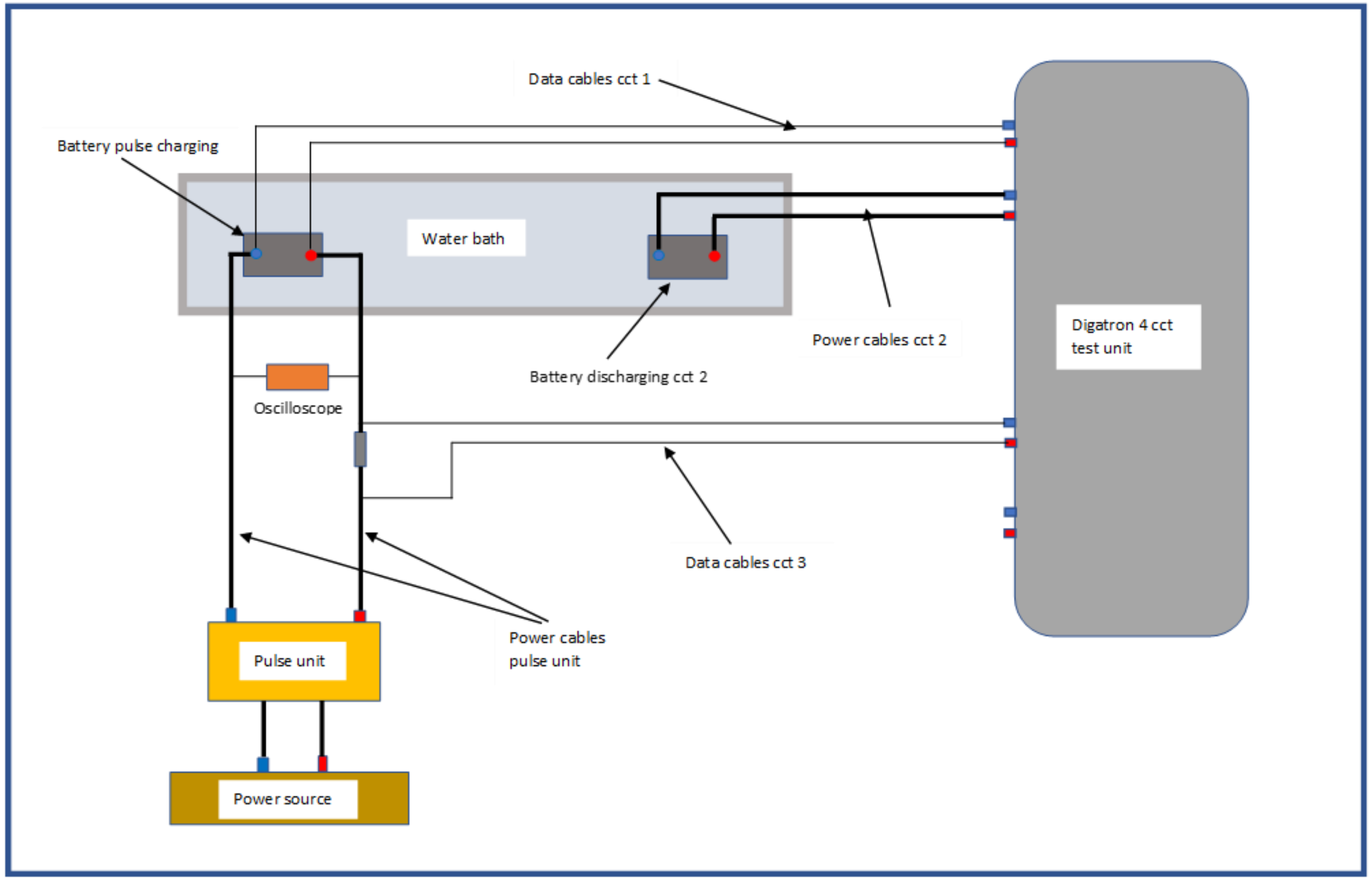
Schematic layout of test equipment including the pulse unit and Digatron test unit



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A 105 Ah 12V LAB standard formation programme supplied by a participating battery manufacturer

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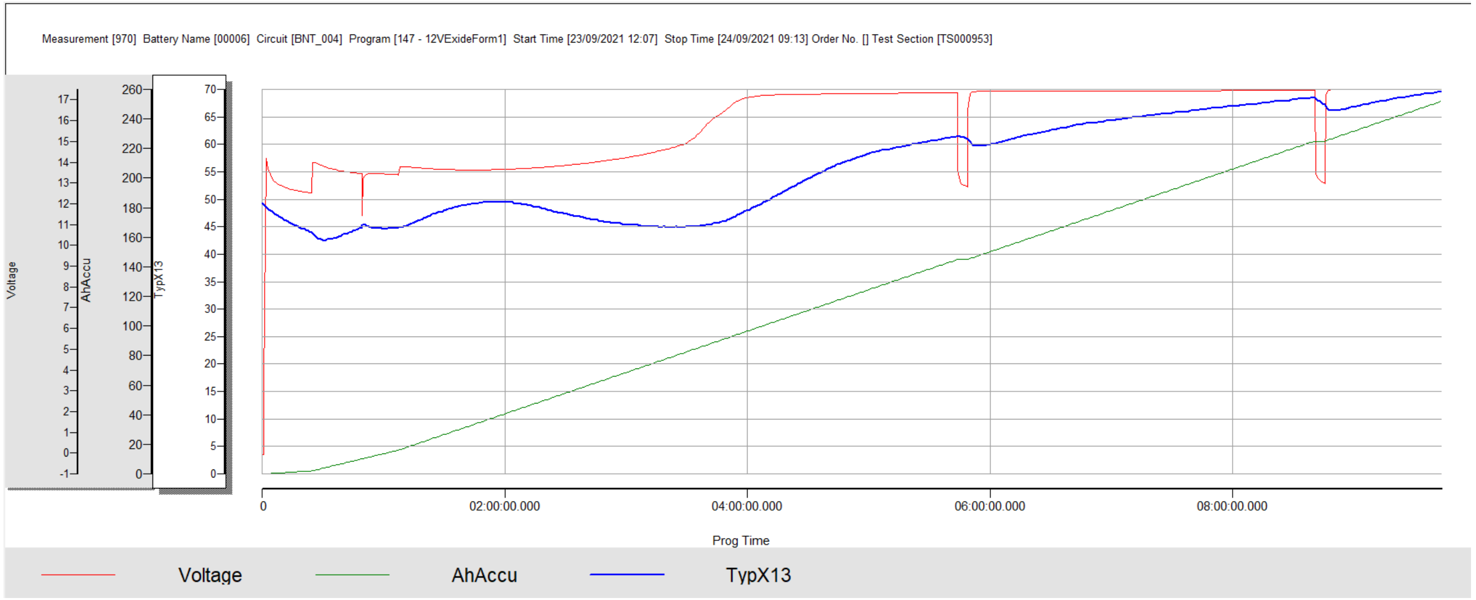
The total formation time, results from a series of CC charge periods and pauses. The pauses and current amplitudes are based on practical experience for controlling the temperature and voltage responses during the programme.

Typical fast charging profile for a low capacity, SLI battery, modified for the Digatron Test Unit



Parasitic reactions that reduce the AM conversion efficiency

positive electrode: $H_2O \longrightarrow \frac{1}{2} O_2 (g) + 2 H^+ + 2 e^-$ V > 2.4 V/cell

negative electrode: $2H^+ + 2 e^- \longrightarrow H2(g)$ V > 2.4 V/cell

Overall cell: $H_2O \longrightarrow \frac{1}{2} O_2 (g) + H_2(g)$

Heat $= I^2R$

Battery formation philosophy of manufacturers:

1. Maximise throughput
2. Control battery temperature by cooling or recirculating electrolyte to reduce damage
3. Put in thicker cable to offset the higher charging currents

These measures actually boost the contribution from the parasitic reactions to further reduce formation inefficiency

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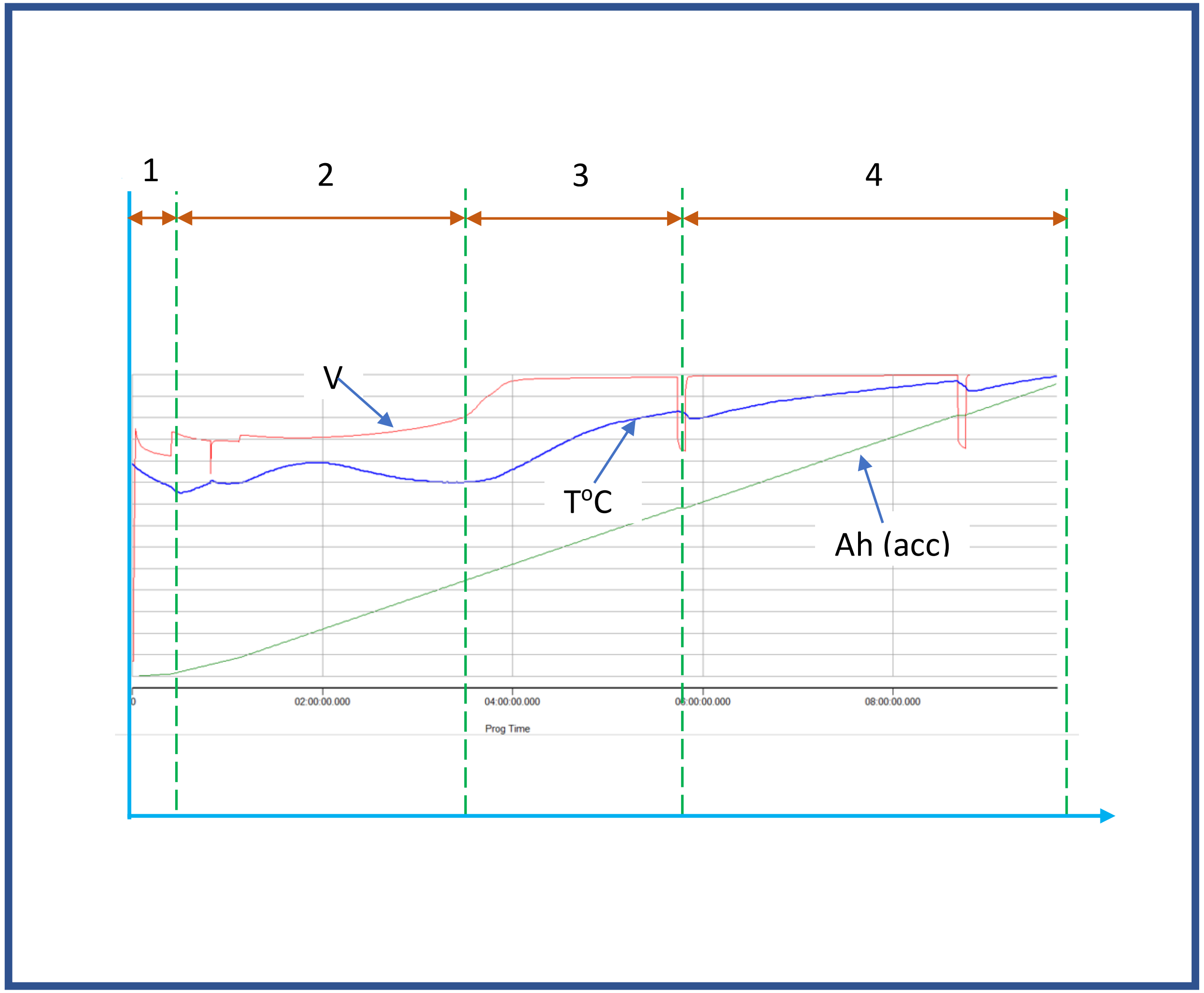
High Efficiency lead acid battery formation

This is a reproduction of a standard programme divided into 4 simplified sections

1. This is the initial phase where the AM/grid interface is formed and the battery resistance drops
2. Is the 2nd phase marking the onset of the conversion of lead sulphates into the formed AM of both plates
3. This third phase is the increasing of the SG of the electrolyte
4. The last phase is the final conversion of the remaining sulphate with an increasing contribution from parasitic reactions



Efficient version of standard formation programme

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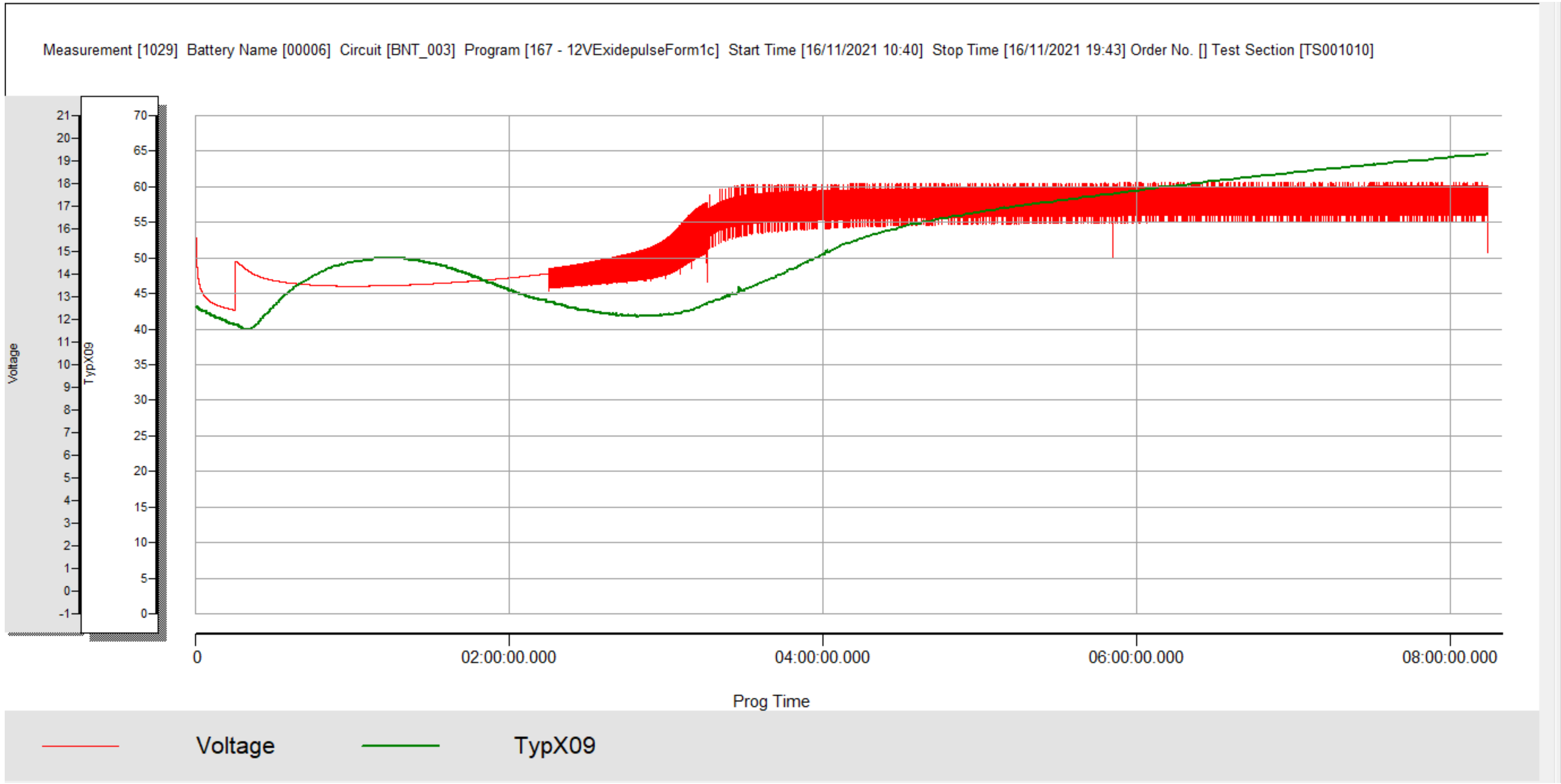
Digatron recording of the result from one of the improved efficiency programmes

This programme uses the information from the standard method to minimise the temperature rises and maximise the current input

The same formation process stages are being followed but the efficiency of the current input is improved

TypX09 is the temperature channel



Results of initial formation energy reduction programmes

High Efficiency lead acid battery formation

Battery number	Formation schedule	Max temp	Max volts	Acc Wh	Acc Ah	Total process time	Discharge test results	Discharge Ah
1	Standard	69.5	17.50	4071	251	10h:38m	5h:35m	62.5
2	Pulsed 1a	71.8	18.05	4158	251	09h:49m	5h:31m	61.8
3	Aborted	Aborted	Aborted	Aborted	Aborted	Aborted	Aborted	Aborted
4	Pulsed 1b1	41	17.79	3302	204	08h:25m	5h:07m	57.4
5	Pulsed 1b2	62	17.92	3261	205	08h:25m	5h:15m	58.8
6	Pulsed 1c	65	17.86	3403	212	08h:14m	5h:25m	60.7

Programme	Battery	Measured Ah @ 5 hr rate	Projected Ah @ 20 h rate (C5 = 0.8xC20)*	Ah @ 20 hr discharge (partner results)
Standard	1	62.5	78.1	73.6
Pulsed 1a	2	61.8	77.3	72.6
Aborted	3	Aborted	N/A	71.3
Pulsed 1b1	4	57.4	71.75	70.4
Pulsed 1b2	5	58.8	73.5	72.5
Pulsed 1c	6	60.7	75.9	70.5

Summary of improved energy efficiency formation results

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Formation schedule	Capacity test results (Ah)	Maximum temperature	% Watt hours saving c.f. standard (%)	Possible increase in production throughput (%)	**Potential energy cost savings for a LAB factory (%)
Standard	62.5	69.5	0	0	0
Pulsed 1a	61.8	71.8	2.1	7.7	1.05
Pulsed 1b1	57.4	41	18.9	11.4	9.5
Pulsed 1b2	58.8	62	20	11.4	10
Pulsed 1c	60.7	65	16.4	13.2	8.4

*Factory capacity results = 56 – 61 Ah
**Formation department energy cost is normally half the total LAB factory energy bill

High Efficiency lead acid battery formation

Summary of formation efficiency trials to March 2022 Current situation

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Savings

1. Formation process time reduced from 10h 38 m to 8h 14 m without capacity loss.

2. Time savings could provide a theoretical output increase of 13%

3. Energy savings were substantial –potential 1.2 million USD for a 10 million SLI LAB factory

4. Additional savings from measures described earlier could double this figure

5. Additional cost savings would include reduced topping up (demineralised water + labour costs) and lower water bath operating temperatures.

Further Work

1. **Establish ideal interrogation pulse profile to identify the precise state of charge for the battery during the formation process**

2. **Devise optimum algorithms for each process step to further minimise the energy use but maximise the Ah input**

3. **Design and build a prototype unit for field trials with participating companies**

4. **Finalise a working pulse unit design for retrofitting to existing Digatron equipment**

5. **Incorporate the hardware and software required into Digatron formation equipment as an energy saving option.**

Contact details

For more information on this presentation or to discuss how your formation costs can be reduced, contact Mark Rigby using the details provided

Alternatively You can visit the UK Powertech stand at this conference

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