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The behaviour of the coup de fouet of valve-regulated lead–acid batteries

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Abstract

This paper presents the results of an investigation into the initial stage of the discharge voltage response of valve-regulated lead–acid (VRLA) batteries. This region is dominated by the phenomenon known as the coup de fouet which manifests itself as a voltage dip followed by a recovery. The research focuses on two parameters found within the coup de fouet region, namely, the trough and the plateau voltage. It is found that these parameters are influenced by the operating conditions and the sate-state-of health (SoH) of the battery. The operating conditions considered are discharge rate, ambient temperature, depth of previous discharge, charge duration, and float voltage. The coup de fouet parameters corresponding to high rate discharges, as well as discharges conducted at low temperatures, have reduced magnitudes compared with those conducted at lower rates or higher temperatures. This behaviour mirrors the availability of capacity when the battery is discharged under the same operating conditions. The float voltage is found to have a direct relationship with the trough and plateau voltages, whereas an indirect relationship between charge duration and the trough and plateau voltages is observed. The influence of variations in discharge depth on the coup de fouet is more complex. For consecutive discharge depths below approximately 10% of rated capacity, the coup de fouet becomes distorted and exhibits a second voltage dip. For consecutive discharges of greater depth, this does not occur. The influence of the degradation in battery SoH due to accelerated thermal ageing, water replenishment post-accelerated thermal ageing, and field ageing is investigated. The coup de fouet parameters associated with the discharge of batteries with low SoH have a reduced magnitude compared with those associated with the discharge of batteries with a high SoH.

Keywords: Coup de fouet; Voltage dip; Capacity; Valve-regulated lead–acid battery; Backup power system

1. Introduction

The start-of-discharge of a valve-regulated lead–acid (VRLA) battery is dominated by two transient voltage responses [1,2]. The first is an electronic response associated with the battery's resistance and inductance [2]. Here, the application of a load causes the voltage to drop suddenly. The voltage quickly recovers within less than 1 ms, depending on the size of the battery [3]. This phenomenon has been targeted by researchers as a means for determining the battery's resistance, and therefore, an indication of capacity [3–5]. Due to the speed of occurrence, however, detection is outside the capabilities of most telecom power systems or battery supervisors. Generally, stand-alone hand-held units have been developed to exploit this phenomenon [3,6].

The second transient response is a more complex phenomenon which is attributed to the electrochemical reactions within the battery and is commonly known as the 'coup de fouet'. The coup de fouet (which translates as 'crack of the whip') occurs whenever a fully charged lead–acid battery is discharged. The coup de fouet region of a Hawker 2HI275 cell discharged at 275 A is shown in Fig. 1(a). The voltage decreases to a minimum, or trough, in a relatively short time. The actual time taken depends on the operating conditions and the state-of-health (SoH) of the battery. The voltage then recovers, to level off at a plateau after a further few minutes, thus, signalling the end of the coup de fouet. Two parameters within the coup de fouet are considered in this investigation: the trough and plateau voltages, as illustrated in Fig. 1(a).

For a fully charged battery, the charge released during a discharge is equal to the capacity of the battery. As stated previously, the coup de fouet only occurs when the battery is fully charged. From this, two issues are raised. First, observing the coup de fouet indicates that the battery is fully charged. Thus, the coup de fouet may be employed as a full

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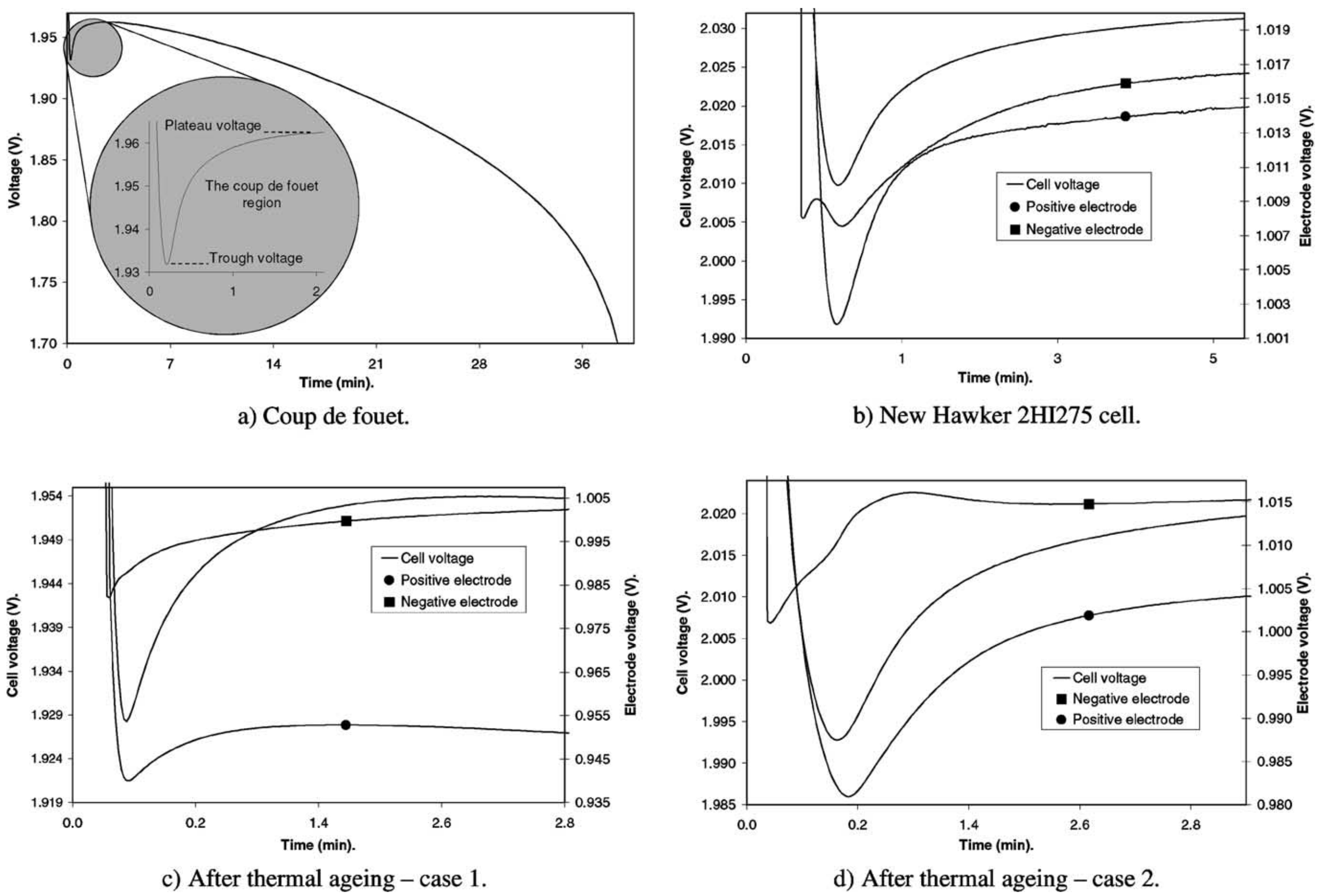


Fig. 1. Coup de fouet and contribution of each electrode to coup de fouet.

charge indicator. Second, any technique relating parameters within the coup de fouet to the charge released by the discharge is actually relating the parameters to battery capacity.

In recent times, very little research has been conducted into the mechanism that is responsible for the coup de fouet. The foremost reference dealing with this phenomenon is over 35 years old [7]. A summarised description of the electrochemical conditions leading up to, and the electrochemical reactions involved in, the occurrence of the coup de fouet can be found in [1]. One of the few recent works has focused on a method of reducing the magnitude of the coup de fouet [8]. In this work, the researchers developed an electrolyte circulation scheme that reportedly reduced the coup de fouet by 57–79% depending on the discharge rate.

The early work [7] reported a negligible contribution to the coup de fouet by the negative electrode while later studies [1,8,9] have reported no contribution at all. Tests conducted using a mercurous sulphate reference electrode have determined that there is a significant contribution to the coup de fouet from the negative electrode. Three situations are illustrated in Fig. 1(b) and (c). Here, the overall cell voltage is given along with the magnitude of the positive and negative electrode voltages. In all cases, the negative electrode appears as dominant as the positive electrode.

No attempt has been made to determine the mechanism responsible for, or the significance of, the negative and positive electrode responses. This would require in-depth electrochemical analysis that is outside the scope of the 'black-box' research performed in this investigation.

The results of studies conducted to determine the relationship between the coup de fouet parameters and operating conditions are presented in Section 2. The operational conditions of discharge rate, ambient temperature, depth of previous discharge, float charge time, and float voltage are considered. Section 3 presents an investigation into the influence of battery SoH the coup de fouet due to accelerated thermal ageing, water addition post-accelerated thermal ageing, and field ageing. Conclusions and the direction of future work are given in Section 4.

2. Influence of operating conditions

In this section, the results of tests conducted to determine the influence of battery operating conditions on the coup de fouet are presented. Preliminary aspects of this work have been presented previously [10,11]. These conditions include: discharge rate, ambient temperature, depth of previous discharge, charge duration, and float voltage. Also

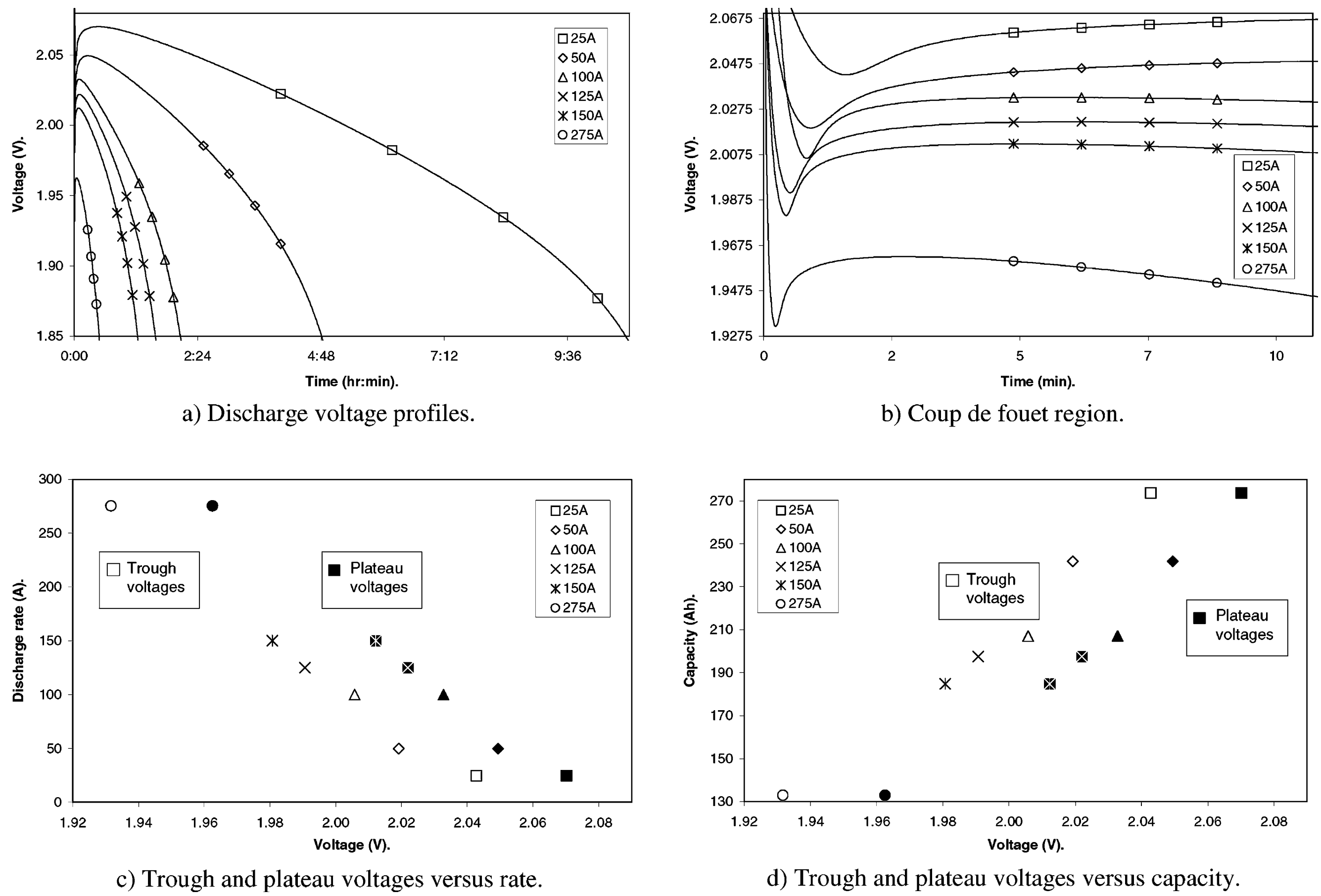


Fig. 2. Discharge of six cells at different constant-current discharge rates.

investigated is the sensitivity of the relationship between the trough and plateau voltages and the capacity.

To examine the coup de fouet region, similar test equipment set-up to that presented in [12] was used. Central to the test equipment is a Hewlett Packard HP34970A Data Acquisition/Switch Unit. This device, which is capable of voltage measurements of up to 20 bits in resolution, was equipped with a 20-channel, differential analogue multiplexor. Using a Visual Basic program, each channel was configured with the appropriate settings to measure voltage, current and temperature. Throughout the tests, the program also controlled the load and charger, via the data acquisition unit, and recorded the data on disc in comma separated text file format. A data-sampling rate of better than 1 Hz (during the coup de fouet region) with a voltage resolution of better than 1 mV was employed.

2.1. Discharge rate and discharge type

The discharge rate has a profound influence on the capacity of a VRLA battery. The relationship between the coup de fouet parameters and discharge rate (as well as the corresponding capacity) was investigated by discharging six Hawker 2HI275 cells at six different rates, namely, 25, 50, 100, 125, 150 and 275 A. The discharges were conducted with an ambient temperature of 20 °C to an end-voltage of 1.85 V per cell. The discharge voltage profiles are illustrated in Fig. 2. The capacity released by the cells varies considerably, from 133 Ah at the 275 A rate to 274 Ah at the 25 A rate (Fig. 2(a)).

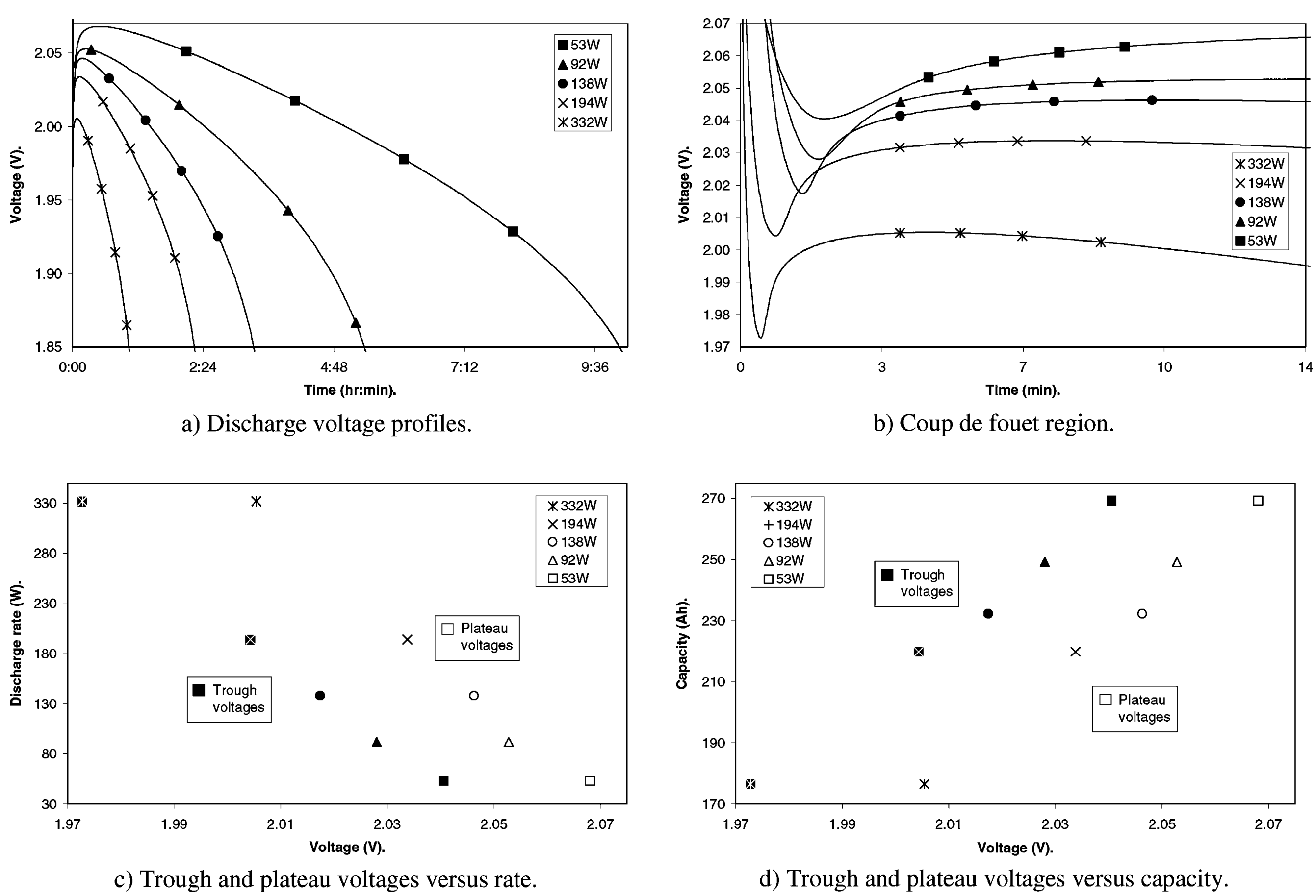
A detailed view of the coup de fouet region is presented in Fig. 2(b). By comparison with Fig. 2(b), it is seen that the higher the discharge rate, corresponding to lower capacity, the lower the trough and plateau voltage. The relationship between the trough and plateau voltage parameters and discharge rate and cell capacity are highlighted in Fig. 2(c) and (d), respectively. In both instances, relationships appear close to linear for both the trough and the plateau voltages.

It has been reported [9] that the coup de fouet is observed for low and medium discharges only. Clearly, this is not the case here. There is no sign of any reduction in magnitude of the coup de fouet for higher rate discharges. This is emphasised by the difference between the trough and the plateau voltages (see Table 1), which ranges from 27 to 32 mV and has no correlation with the discharge rate.

It is apparent from Fig. 2(b) that the time of occurrence of the trough and plateau voltages is inversely related to the discharge rate. That is, the trough and plateau voltages occur after a relatively short time from the start-of-discharge for discharges conducted at a high rate, while the occurrence is delayed considerably for lower rate discharges. In addition,

Table 1
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharges of different rates and types

Discharge (rate/capacity)	Trough occurrence			Plateau occurrence			Plateau − trough difference (V)
	Time (s)	Charge released		Time (s)	Charge released		
		Ah	%		Ah	%	
25 A/274 Ah	96	0.682	0.249	1616	11.459	4.185	0.027
50 A/242 Ah	53	0.752	0.311	955	13.331	5.512	0.030
100 A/207 Ah	53	1.478	0.714	346	9.652	4.660	0.027
125 A/198 Ah	30	1.039	0.526	361	12.535	6.345	0.031
150 A/185 Ah	24	0.997	0.539	292	12.156	6.579	0.032
275 A/132 Ah	12	0.913	0.687	165	12.558	9.445	0.031
53 W/269 Ah	126	0.901	0.335	1856	12.471	4.631	0.033
92 W/249 Ah	117	1.447	0.580	898	10.613	4.259	0.029
138 W/232 Ah	92	1.705	0.734	656	12.273	5.285	0.029
194 W/220 Ah	51	1.344	0.611	474	12.144	5.524	0.025
332 W/177 Ah	29	1.341	0.759	297	12.675	7.179	0.027
0.067 Ω/263 Ah	96	0.810	0.307	1884	14.634	5.555	0.031
0.038 Ω/252 Ah	76	1.124	0.446	874	12.852	5.099	0.031
0.026 Ω/226 Ah	50	1.071	0.474	626	13.473	5.960	0.032
0.018 Ω/209 Ah	35	1.076	0.515	447	13.823	6.616	0.029
0.0143 Ω/198 Ah	33	1.280	0.646	350	13.243	6.684	0.028



a) Discharge voltage profiles. b) Coup de fouet region.

c) Trough and plateau voltages versus rate. d) Trough and plateau voltages versus capacity.

Fig. 3. Discharge of five cells at different constant-power discharge rates.

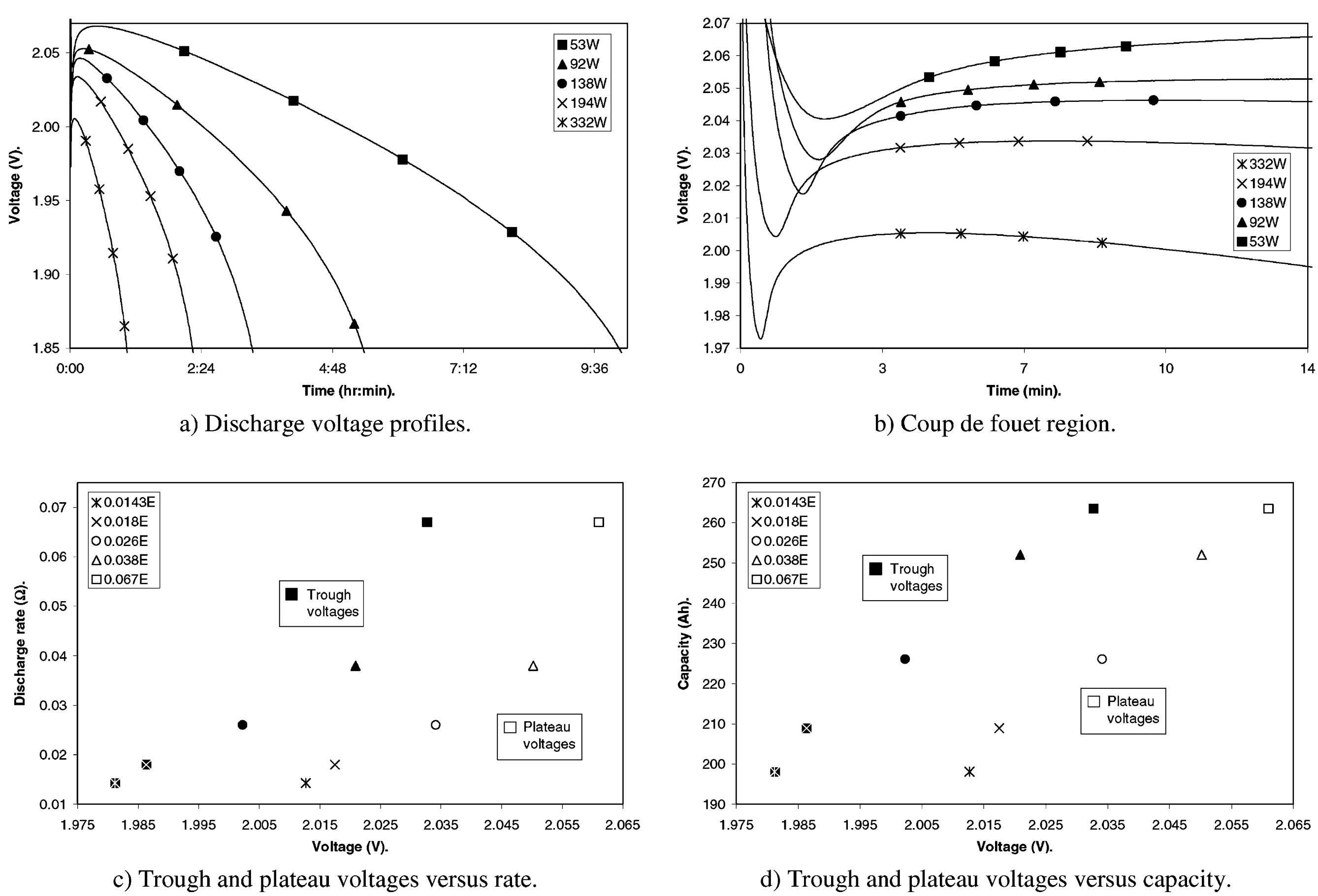
the charge released by the time the trough and plateau voltages occur is relatively consistent between tests (regardless of rate). For the trough voltage parameter, the minimum charge released was 0.7 Ah and the maximum was 1.5 Ah (with an average of 1 Ah), while for the plateau voltage parameter the minimum charge released was 9.7 Ah and the maximum was 13.3 Ah (with an average of 11.7 Ah). The charge released and the discharge elapse times corresponding to the occurrence of the trough and plateau voltage, for each discharge, are given in Table 1.

The influence of variations in constant-power discharge rates on the coup de fouet is illustrated in Fig. 3. Five Hawker 2HI275 cells were discharged at constant-power rates of 53, 92, 138, 194 and 332 W. As earlier, the discharges were conducted with an ambient temperature of 20 °C to an end-voltage of 1.85 V per cell.

The entire discharge voltage versus time characteristics are illustrated in Fig. 3(a). For constant-power discharge, the capacity of the cells varied from 177 Ah for the 332 W (45 min) rate to 269 Ah for the 53 W (9 h) rate (see Table 1). A detailed view of the coup de fouet region is given in Fig. 3(b). Again by comparison of Fig. 3(a) and (b): the higher the discharge rate, which corresponds to lower capacity, the lower the trough and plateau voltage.

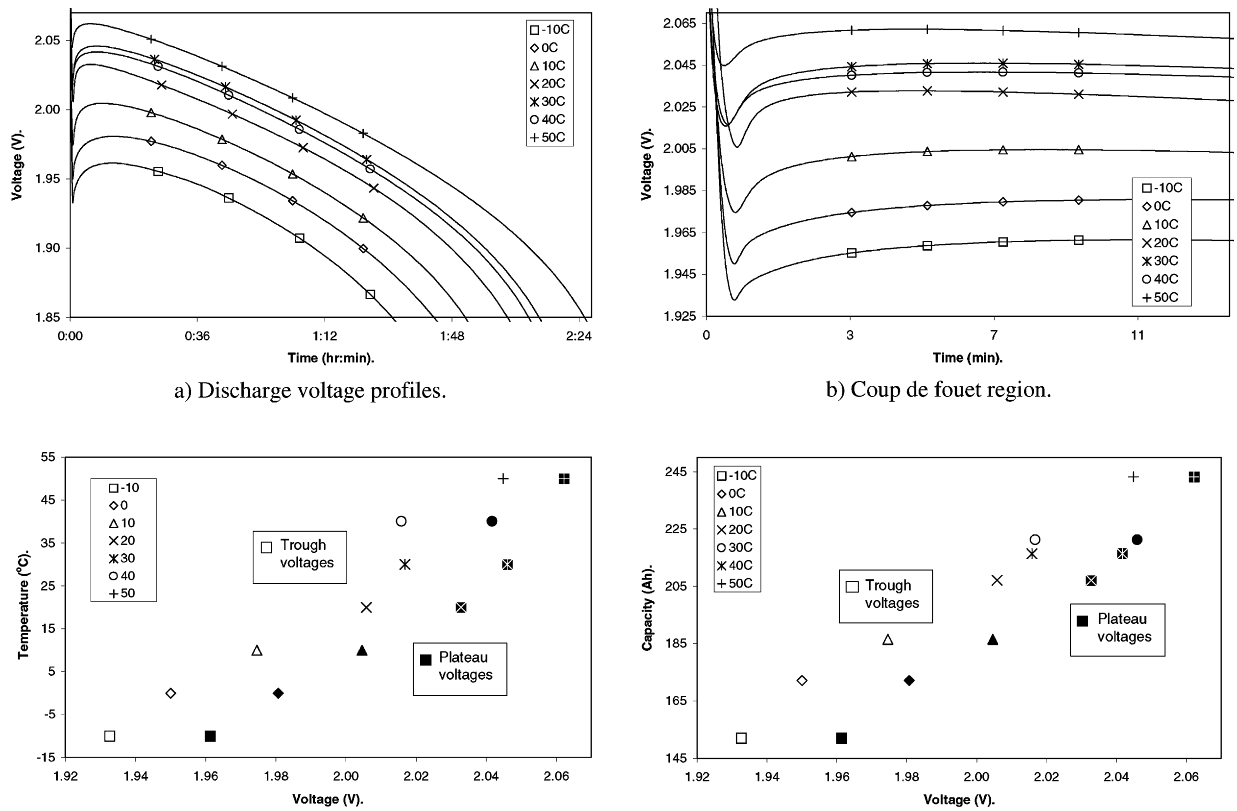
Following the previous results for variations in constant-current discharge rates, the magnitude of the constant-power discharge rate is inversely related to the occurrence time of the trough and plateau voltages (see Table 1). Furthermore, from Fig. 3(c), the relationship between the trough and plateau voltage parameters and the constant-power discharge rates is close to linear. The relationship between the capacity and the trough and plateau voltage parameters is, again, also close to linear as illustrated in Fig. 3(d).

The influence of variations in constant-resistance discharge rates completes the investigation of the influence of discharge rate on the coup de fouet. Five Hawker 2HI275 cells were discharged at constant-resistance rates of 0.0143, 0.018, 0.026, 0.038 and 0.067 Ω. As earlier, the discharges were conducted at an ambient temperature of 20 °C to an end voltage of 1.85 V per cell. The entire discharge voltage versus time characteristics are illustrated in Fig. 4(a). A detailed view of the coup de fouet region is given in Fig. 4(b). The capacity of the cells varied from 198 Ah for the 0.0143 Ω rate to 263 Ah for the 0.067 Ω rate (see Table 1). Again, from a comparison of Fig. 4(a) and (b), the higher the discharge rate, which corresponds to lower resistance and lower capacity, the lower the trough and plateau voltages.



a) Discharge voltage profiles.
b) Coup de fouet region.
c) Trough and plateau voltages versus rate.
d) Trough and plateau voltages versus capacity.

Fig. 4. Discharge of five cells at different constant-resistance discharge rates.



a) Discharge voltage profiles.

b) Coup de fouet region.

c) Trough and plateau voltages versus temperature.

d) Trough and plateau voltages versus capacity.

Fig. 5. Discharge of six cells with various ambient temperatures.

Following on from the results obtained earlier, the relationship between the constant-resistance discharge rates and the trough and plateau voltage parameters is, again, close to linear, as illustrated in Fig. 4(c). The close to linear relationship between the trough and plateau voltage parameters and capacity, is shown in Fig. 4(d).

The discharge elapse times and charge released corresponding to the occurrence of the trough and plateau voltage parameters are listed in Table 1 discharge tests conducted at constant-current, power and resistance rates. The percentage charge released is given with respect to the capacity of the cell when discharged to an end voltage of 1.85 V.

2.2. Ambient temperature

Temperature is another major influence on battery capacity. In general, the battery temperature can only be controlled indirectly by controlling the ambient temperature. Thus, ambient temperature is used as the control variable to determine the influence of battery temperature on the coup de fouet. To this end, seven Hawker 2HI275 cells were discharged at a rate of 100 A with ambient temperatures of −10, 0, 10, 20 30, 40 and 50 °C.

The entire discharge voltage profiles are given in Fig. 5(a) and the coup de fouet regions are given in detail in Fig. 5(b). In this case, the range of cell capacity is from 152 Ah at −10 °C to 243 Ah at 50 °C. By inspection of the discharge voltage profiles, the influence of temperature is clear. The lower the temperature, the lower the start voltage which reflects the lower capacity available.

The relationship between the trough and plateau voltages and temperature is illustrated in Fig. 5(c). It appears that the relationship is close to linear with one obvious exception, namely, the 40 °C case. By inspection of Fig. 5(d), which illustrates the relationship between the trough and plateau voltages and capacity, it can be seen that the cell discharged at 40 °C has less capacity than the cell discharged at 30 °C. Thus, the discrepancy in the relationship depicted in Fig. 5(c) is due to the influence of reduced cell capacity (SoH).

By close inspection of Fig. 5(b), it is apparent that the time of occurrence of the trough voltages is inversely related to the ambient temperature. That is, in general, the trough voltage occurs after a relatively short time from the start-of-discharge for discharges conducted at a high ambient temperatures, while the occurrence is delayed at lower ambient temperatures. This relationship is not as obvious as in the case of discharge rate variation due to the much greater range in discharge rates utilised.

The discharge elapse times and charge released corresponding to the occurrence of the trough and plateau voltage parameters are given in Table 2. Again, the percentage charge released is given with respect to the capacity of the cell determined when discharged to an end voltage of 1.85 V. The decrease in charge released corresponding to the

Table 2
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharges at different ambient temperatures

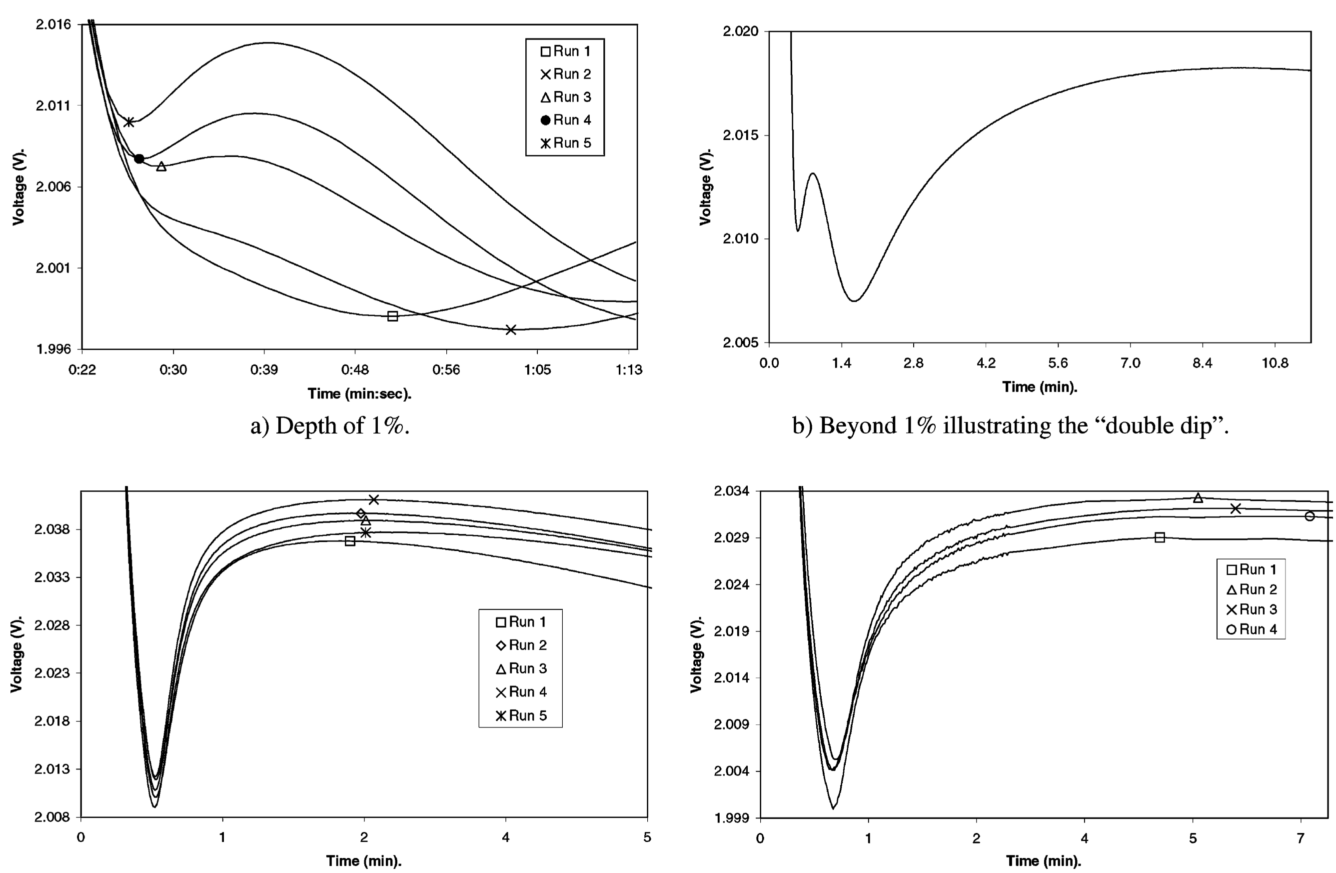
Discharge (°C/capacity, Ah)	Trough occurrence			Plateau occurrence			Plateau − trough difference (V)
	Time (s)	Charge released		Time (s)	Charge released		
		Ah	%		Ah	%	
−10/152	44	1.222	0.803	646	17.959	11.810	0.029
0/172	44	1.223	0.710	715	19.921	11.569	0.031
10/187	46	1.278	0.685	542	15.076	8.085	0.030
20/207	49	1.367	0.660	345	9.624	4.647	0.027
30/221	33	0.916	0.414	435	12.092	5.466	0.029
40/216	30	0.833	0.385	445	12.373	5.717	0.026
50/243	27	0.750	0.308	329	9.146	3.759	0.017

occurrence of the trough voltage as the ambient temperature increases is clear, although the coup de fouet corresponding to discharges conducted at 10 and 20 °C does not comply. The relationship between occurrence time (and charge released) corresponding to the plateau voltage and ambient temperature is less conclusive.

Also given in Table 2 is the difference between the plateau and trough voltages for each discharge. For all discharges except the one conducted at 50 °C ambient temperature, this voltage difference is relatively constant.

2.3. Depth of previous discharge

The depth of previous discharge has a dual influence on the coup de fouet, i.e. both the shape and magnitude are affected. This is illustrated in Fig. 6 which shows consecutive discharge voltage versus time characteristics of a Hawker 2HI275 cell discharged 2 Ah at a rate of 100 A and an ambient temperature of 20 °C. The cell was recharged, in all cases, for a fixed time of 24 h. The cell was found to deliver approximately 200 Ah to an end voltage of 1.85 V when



a) Depth of 1%. b) Beyond 1% illustrating the “double dip”. c) Depth of 12.5%. d) Depth of 100%.

Fig. 6. Influence of previous discharge on coup de fouet region.

discharged at a rate of 100 A. Thus, a 2 Ah discharge corresponds to a depth-of-discharge (DoD) of approximately 1%.

The first discharge was terminated just past the trough voltage. The next discharge was similarly terminated, but the coup de fouet discharge voltage characteristic was altered. In descending to the trough voltage, the voltage characteristic is much flatter. From close inspection, it can be seen Fig. 6(a) that there is a small rise in voltage at approximately 40 s into the discharge. This voltage rise before the trough voltage is more obvious in the following discharge. In fact, it appears that an additional trough and plateau voltage occurs before the occurrence of the original trough voltage. The additional dip becomes even more significant in the remaining discharges. The discharge voltage characteristics of a discharge that is allowed to continue past the 2 Ah (1%) DoD limit us shown in Fig. 6(b). Clearly, a double voltage dip occurs. This phenomenon has also been observed with batteries that are discharged after being left at open-circuit for a long period [10].

A similar affect to that illustrated in Fig. 6(a) was observed for discharges up to a depth of approximately 10%. The significance of the second dip reduces, however, as the depth of consecutive discharges increases. For consecutive discharges to a depth of greater than approximately 10%, the second dip is no longer present. By way of example Fig. 6(c) and (d) illustrate the coup de fouet region for discharges of 12.5 and 100% DoD, respectively. The recharging between tests consisted of applying 110% of the charge released during the previous discharge to the cell and then float charging for 24 h. Clearly, no double dip occurs. Furthermore, the coup de fouet regions of each consecutive discharge are very consistent. In the case of discharges to 12.5% DoD, the range in trough and plateau voltages is 3.2 and 4.3 mV, respectively, and for 100% DoD, the range in trough and plateau voltages is 5.3 and 4.3 mV, respectively. It is interesting to note that for the full discharges shown in Fig. 6(d), the first discharge was conducted after a full discharge whose coup de fouet region is given in Fig. 6(b). Given that the first discharge of Fig. 6(d) is the most inconsistent in this series, it is still (partially) affected by the previous discharges.

The values of the trough and plateau voltages corresponding to consecutive discharges of 100 and 12.5% DoD vary by approximately 5 mV, respectively. In both cases, the difference between the plateau and trough voltage is similar at approximately 30 mV. Furthermore, the occurrences of both the trough and plateau voltages appear to be delayed for consecutive discharges of 100% DoD compared with those for consecutive discharges of 12.5% DoD.

Despite these observations, it is difficult to draw any definitive relationship between the coup de fouet parameters and the previous DoD. Due to the variations in the depth of the previous discharge, the cell requires different amounts of recharge (due to different amounts of charge being released). Hence, it is impossible to de-couple the influence of the different charge durations (see next section) from the influence of different previous discharge depths.

2.4. Charge duration

Although it is difficult to quantify the influence of previous discharge depth due to the interference of the influence of recharge duration, it is possible to determine the influence of recharge duration alone. The dependence of the trough and plateau parameters on charge time are illustrated in Fig. 7. This data was obtained by consecutive discharges of a Hawker 2HI275 cell after various periods of charge. The discharge depth in all cases is 12.5% of rated capacity, the discharge rate is 100 A, and the ambient temperature is 20 °C. Thus, with consistent rate, temperature and previous discharge depth, a consistent influence is applied to the coup de fouet by these operating conditions. The only operating condition to vary, and therefore have a varying influence on the coup de fouet, is charge duration. This is shown in Fig. 7(a). The trough region is illustrated in greater detail in Fig. 7(b) where it can be seen that for a longer charge duration, a lower the trough voltage results. As the charge duration increases, however, the decrease in the coup de fouet parameter becomes less. Thus, it is envisaged that the relationship between the trough and plateau voltages and charge duration is similar to an exponential relationship as depicted in Fig. 7(c) and (d), respectively.

The occurrences of the trough and plateau voltages, given in Table 3, are delayed slightly for discharges conducted after a longer duration of charge. As the discharges are not completed to the end voltage, the charge released corresponding to the occurrence of the trough and plateau voltages is not given as a percentage of total charge released (capacity). The difference between the trough and plateau voltages, also given in Table 3, is reasonably constant at approximately 30 mV regardless of the charge duration.

2.5. Float voltage

At an ambient temperature of 20 °C, the rated float voltage of the Hawker 2HI275 cell is 2.27 V per cell. The coup de fouet region for several 100 A discharges at 20 °C ambient temperature to a depth of 12.5% is shown in Fig. 8. Five float voltages of 2.22, 2.27, and 2.32, 2.37 and 2.47 V were used to charge the cell for a fixed duration. From Fig. 8(b), it appears that there is a close to linear relationship between the trough and plateau voltages and float voltage for float voltages from 2.2 to 2.32 V. For higher float voltages, the trough and plateau voltages reach a maximum. Conversely, float voltages lower than 2.2 V result in an undercharging of the cell and, consequently, an absence of the coup de fouet.

For higher float voltages, the occurrence time of the trough voltage is, in general, earlier. By contrast, for the plateau voltages it is delayed. These occurrence times are given in Table 4 along with the difference between the trough and plateau voltage, which remains relatively constant. As the

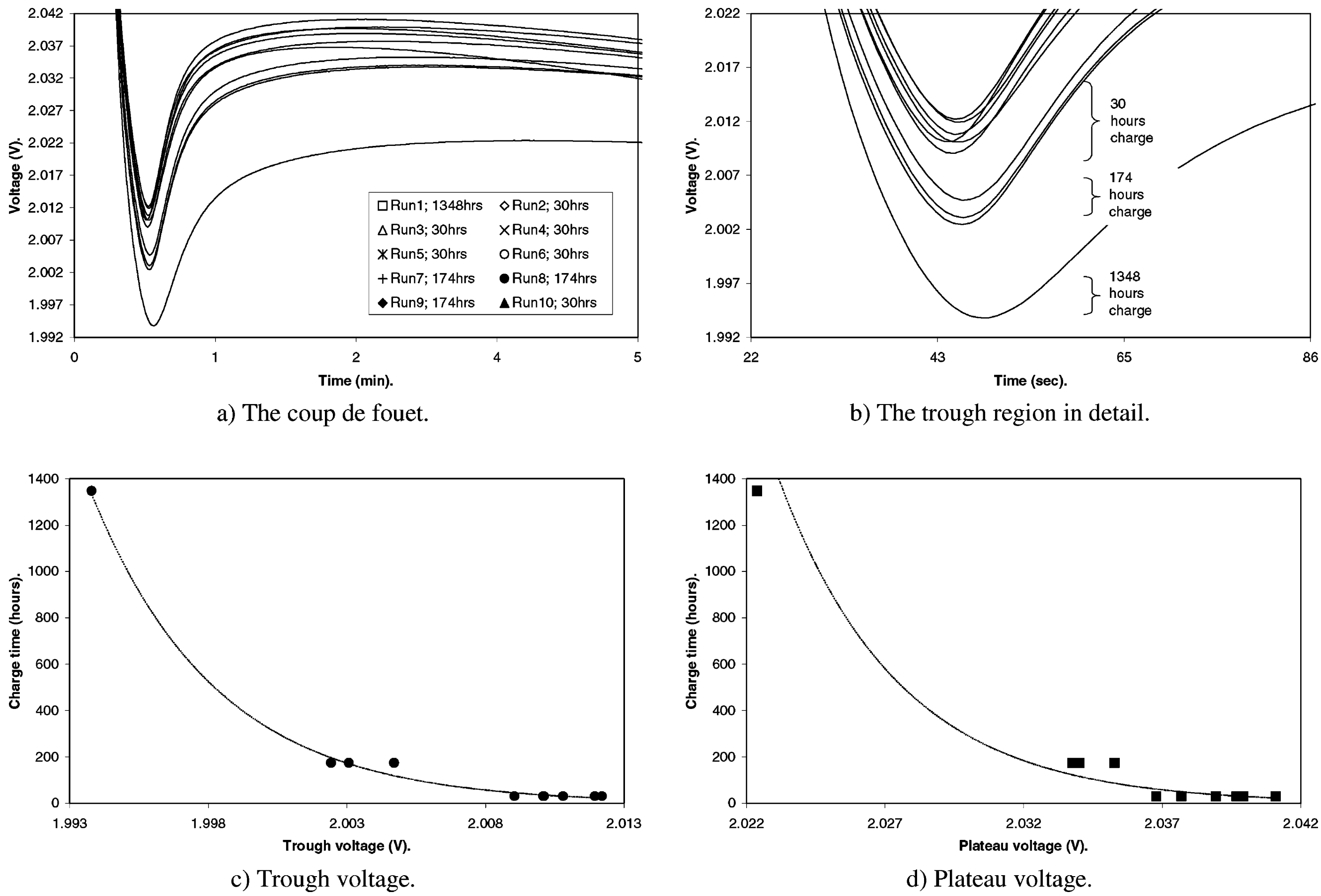


Fig. 7. Relationship between trough and plateau voltages and charge time.

Table 3
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharges conducted after charging for different durations

Discharge (charge duration, h)	Trough occurrence		Plateau occurrence		Plateau − trough difference (V)
	Time (s)	Charge released (Ah)	Time (s)	Charge released (Ah)	
30	43	2.472	172	9.781	0.029
30	43	2.476	169	9.612	0.028
30	43	2.479	172	9.808	0.028
30	43	2.474	177	10.073	0.029
30	42	2.408	187	10.669	0.030
30	43	2.471	162	9.247	0.027
174	44	2.520	210	11.967	0.031
174	44	2.529	215	12.230	0.031
174	44	2.523	218	12.436	0.031
1348	47	2.684	273	15.454	0.029

discharges are not completed to the end voltage, the charge released corresponding to the occurrence of the trough and plateau voltages is not given as a percentage of total charge released (capacity).

2.6. *Sensitivity of operating conditions*

The sensitivities of the trough and plateau voltage parameters to the operating conditions investigated are listed in Table 5. This data is valid for the Hawker 2HI275 cell investigated. In general, the discharge rate will be the most dominant operating condition, as the scope for variation is much greater. Discharge rate can be defined in terms of current, power or resistance. The sensitivity of the coup de fouet to discharge rate defined in terms of resistance is very large. This may be misleading as the resistance changes by very small amounts (in the order of mΩ) to effect a significant change in discharge rate.

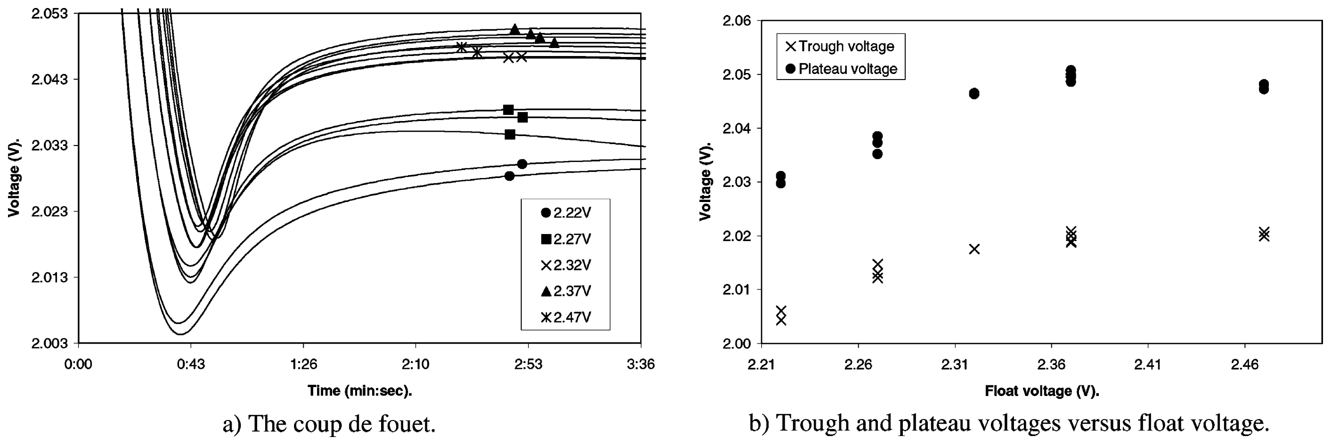


Fig. 8. Influence of float voltages.

Table 4
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharges conducted after charging at different float voltages

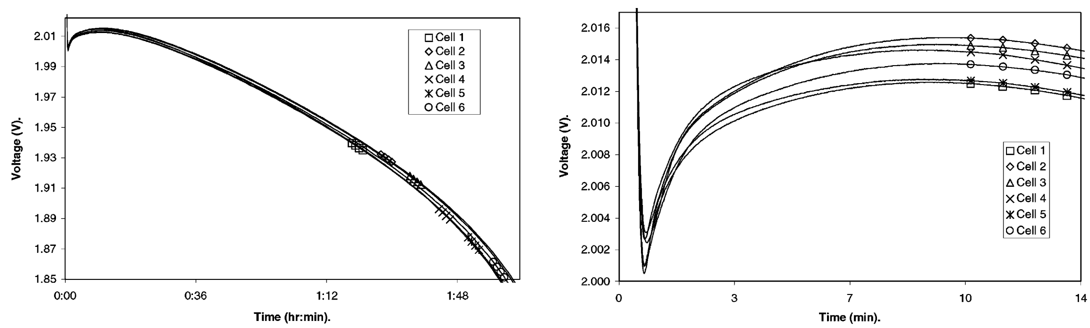
Discharge (float voltage, V/test number)	Trough occurrence		Plateau occurrence		Plateau − trough difference (V)
	Time (s)	Charge released (Ah)	Time (s)	Charge released (Ah)	
2.22/1	36	1.009	263	7.371	0.025
2.22/2	37	1.038	267	7.490	0.025
2.27/1	41	1.150	130	3.621	0.020
2.27/2	41	1.150	164	4.581	0.024
2.27/3	41	1.148	183	5.134	0.026
2.32/1	44	1.231	181	5.074	0.029
2.32/2	43	1.202	174	4.874	0.029
2.37/1	51	1.426	183	5.125	0.030
2.37/2	49	1.374	194	5.454	0.030
2.37/3	48	1.345	192	5.396	0.030
2.37/4	47	1.317	195	5.479	0.030
2.47/1	45	1.260	178	4.995	0.027
2.47/2	44	1.232	172	4.827	0.027

The second most dominant operating condition is ambient temperature. The remaining operating conditions of previous discharge depth, charge duration and float charge voltage have, in comparison, a negligible effect on the coup de fouet.

Note that, a negative sensitivity indicates that the change in coup de fouet parameter is in the opposite direction to the change in operating condition (that is, they are inversely related).

Table 5
Sensitivity of trough and plateau voltage parameters to operating conditions for Hawker 2HI275 cell

Operating condition	Range	Capacity		Trough voltage		Plateau voltage	
		Range (Ah)	Sensitivity	Range (mV)	Sensitivity	Range (mV)	Sensitivity
Constant-current discharge rate	25–275 A	133–274	0.56 Ah/A	115	−0.46 mV/A	110	−0.44 mV/A
Constant-power discharge rate	53–332 W	177–269	0.33 Ah/W	68	−0.24 mV/W	63	−0.23 mV/W
Constant-resistance discharge rate	0.0143–0.067 Ω	198–263	1233.4 Ah/Ω	51	967 mV/Ω	48	911 mV/Ω
Ambient temperature	−10–50 °C	152–243	1.52 Ah/°C	115	1.92 mV/°C	98	1.63 mV/°C
Previous discharge depth	12.5–100%	NA	NA	5	−0.06 mV/%	10	−0.11 mV/%
Charge duration	24–144 h	NA	NA	10	−0.08 mV/h	12	−0.1 mV/h
Float charge voltage	2.22–2.32 V	NA	NA	10	0.1 mV/mV	15	0.15 mV/mV



a) Discharge voltage profiles. b) Coup de fouet region.

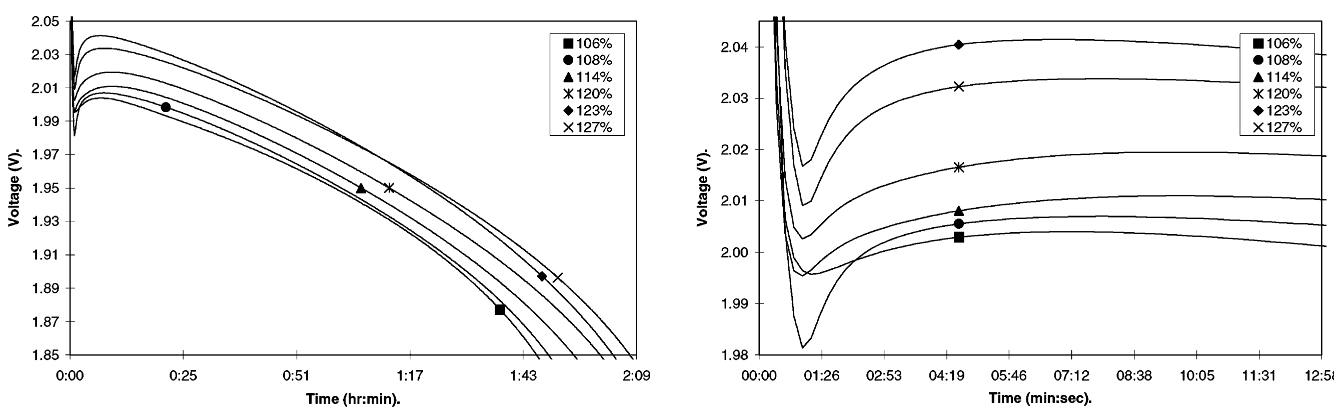
Fig. 9. Discharge at 100 A to an end voltage of 1.85 V per cell of six Hawker 2HI275 cells configured as 12 V string.

3. Influence of battery conditions

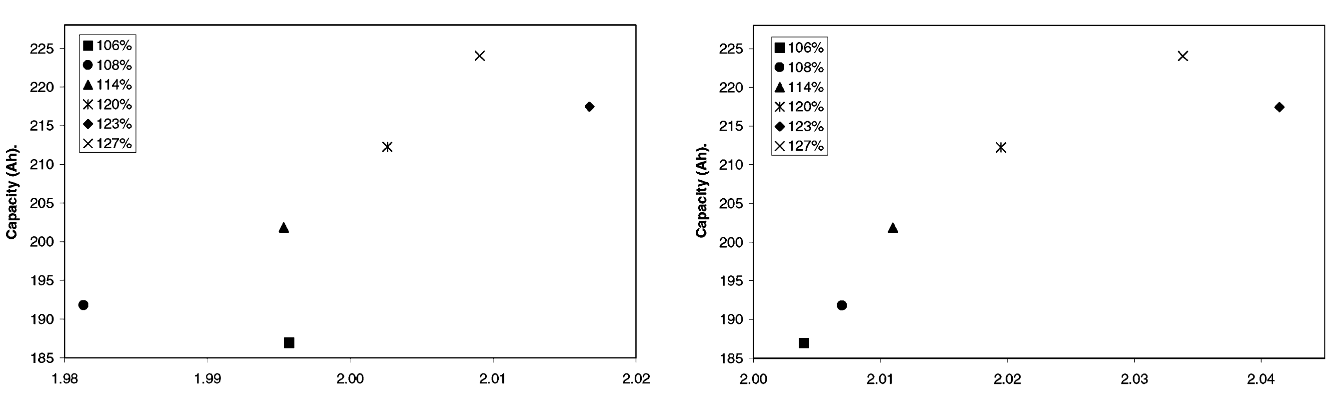
This section investigates the influence of battery condition on the coup de fouet due to accelerated thermal ageing [11], water replenishment post thermal ageing, and field ageing. To establish a benchmark, the sensitivity of the relationship between the trough and plateau voltage parameters and the capacity of new cells is investigated first.

3.1. New cells

To determine the sensitivity of the relationship between the trough and plateau voltage parameters and capacity, six new Hawker 2HI275 cells were discharged together as a 12 V string. The discharge rate was 100 A, the ambient temperature was 20 °C, and the end voltage was 1.85 V per cell. The entire discharge voltage profiles are shown in Fig. 9(a). The discharge lasted approximately 2 h with



a) Discharge voltage characteristics. b) Coup de fouet region.



c) Trough voltage versus capacity. d) Plateau voltage versus capacity.

Fig. 10. Influence of field ageing on coup de fouet of Hawker 2RG310 cell.

Table 6
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharge of field-aged cells

Discharge (% capacity)	Trough occurrence			Plateau occurrence			Plateau − trough difference (V)
	Time (s)	Charge released		Time (s)	Charge released		
		Ah	%		Ah	%	
106	72	2.080	1.112	420	12.137	6.492	0.008
108	60	1.733	0.903	468	13.525	7.051	0.026
114	66	1.733	0.858	564	16.301	8.075	0.016
120	60	1.733	0.816	552	15.954	7.516	0.017
123	60	1.733	0.797	420	12.137	5.581	0.025
127	60	1.733	0.773	468	13.525	6.037	0.025

each cell reaching the end voltage within 4 min of each other. The coup de fouet region is shown in detail in Fig. 9(b).

The capacity of these cells are very uniform, only 6.3 Ah (or 3.1% of the average 201.9 Ah capacity) separates the capacity of the worst and best cell. The corresponding spread in both trough and plateau voltage is approximately 3 mV. With such a small range in capacity, any relationship between the trough and plateau voltages and cell capacity is less than conclusive. It is interesting to note, however, that in general the lower the trough and plateau voltage, the lower the cell capacity.

3.2. Field ageing

The discharge voltage versus time characteristics of six field-aged cells are given in Fig. 10(a). These 5-year-old Hawker 2RG310 cells have been employed in a power system test in a room where the temperature is routinely above 40 °C and they have undergone rigorous cycling. The cell type very similar to the Hawker 2HI275 cell with the main difference being the material used to construct the container.

On discharging at a constant-current rate of 100 A and an ambient temperature of 20 °C to an end voltage of 1.85 V, the range in capacity is 106–127% of the manufacturer's rated capacity. The coup de fouet region is given in detail in Fig 10(b). The relationship between the capacity and the trough and the plateau voltage parameters is shown in Fig. 10(c) and (d), respectively. In both cases, the relationships are close to linear.

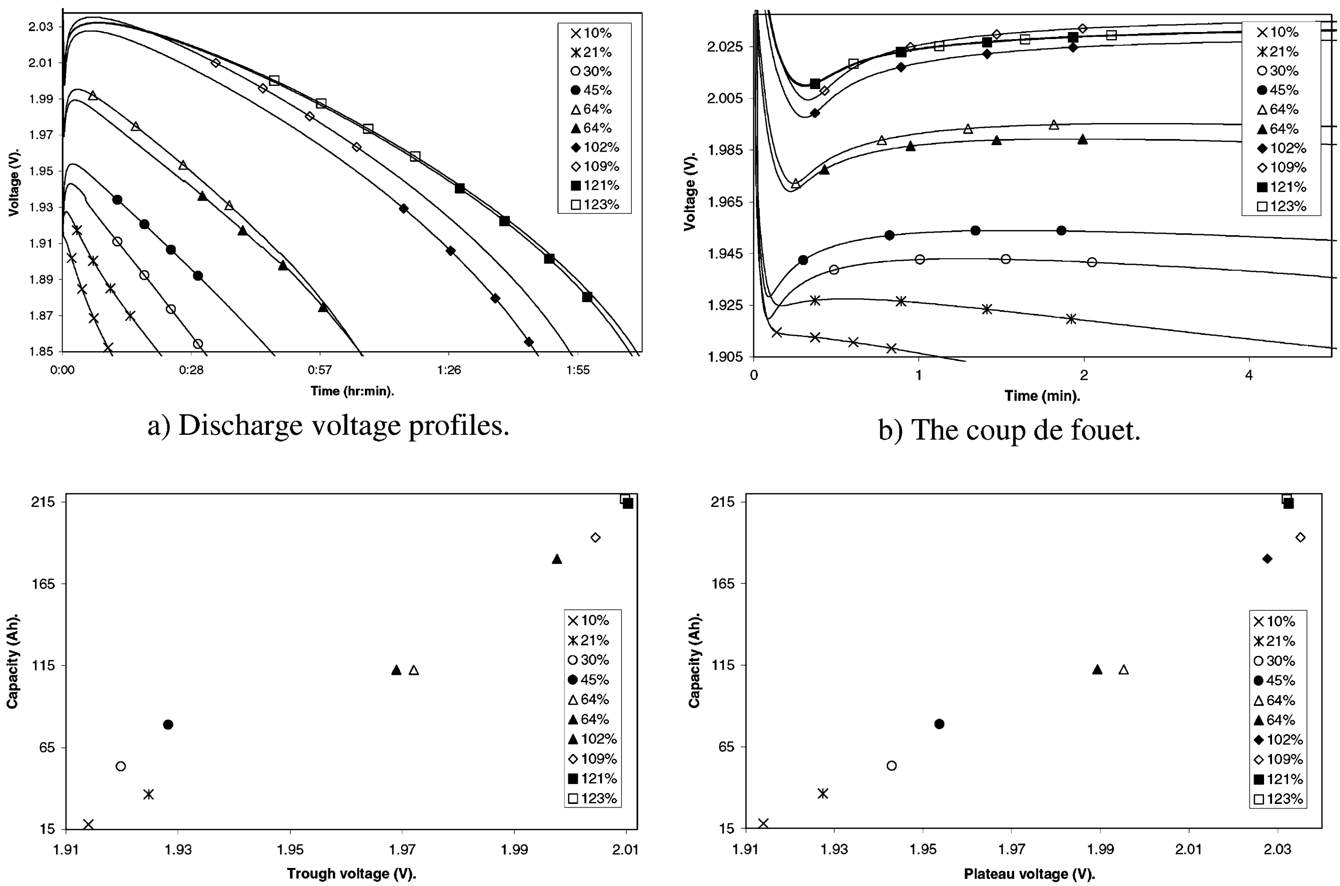
The discharge elapse times and charge released corresponding to the occurrence of the trough and plateau voltages are given in Table 6, together with the difference between the plateau and trough voltage. The trough occurrence time is reasonably consistent between all cells and, subsequently, so is the charge released. No such behaviour is evident with the plateau voltage. The difference between the plateau and trough voltages, is, in general, lower for cells of lower capacity (Table 6).

3.3. Accelerated thermal ageing

The thermal ageing a batteries is a common practice of battery manufacturers for rating operational life [13]. The experiment was conducted by charging four pairs of new

Table 7
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharge of cells with low SoH due to accelerated thermal ageing

Discharge (% capacity)	Trough occurrence			Plateau occurrence			Plateau − trough difference (V)
	Time (s)	Charge released		Time (s)	Charge released		
		Ah	%		Ah	%	
123	26	0.748	0.345	460	12.844	5.920	0.022
121	25	0.720	0.336	450	12.565	5.864	0.022
109	28	0.812	0.420	381	10.748	5.560	0.031
102	26	0.756	0.420	367	10.352	5.745	0.030
64	18	0.531	0.471	162	4.530	4.025	0.020
64	20	0.586	0.522	202	5.679	5.052	0.023
45	7	0.223	0.283	110	3.098	3.924	0.026
30	7	0.223	0.418	109	3.070	5.748	0.023
21	13	0.394	1.083	47	1.350	3.713	0.003
10	13	0.394	2.180	13	0.394	2.180	0.000



a) Discharge voltage profiles. b) The coup de fouet. c) Trough voltage versus capacity. d) Plateau voltage versus capacity.

Fig. 11. Influence of SoH degradation due to accelerated thermal ageing.

Hawker 2HI275 cells at the nominal 20 °C float voltage of 2.27 V and an ambient temperature of 71 °C for various periods. After discharging at a rate of 100 A to an end voltage of 1.85 V, the cells exhibited capacities between 10 and 123% of the manufacturer's rated capacity (177 Ah), see Table 7.

The entire discharge voltage profiles of each pair of cells are given in Fig. 11(a) and close ups of the coup de fouet for the discharges are shown in Fig. 11(b). Clearly, the cells which have the lowest capacity have a lower coup de fouet (trough and plateau voltages). The relationship between the capacity due to the thermal ageing and the trough and plateau voltages is illustrated in Fig. 11(c) and (d), respectively. In both cases, the relationship is close to linear. This is emphasised by the correlation coefficients of 0.979 and 0.981 for the trough and plateau voltage parameters, respectively. Furthermore, the resolution of capacity with the trough and plateau parameters is similar at approximately 1.8 Ah/mV (or 1%/mV) and 1.5 Ah/mV (or 0.9%/mV), respectively.

The cell capacities are given in Table 7, along with the trough and plateau voltage occurrence times and the corresponding charge released. Also given is the difference between the plateau and trough voltages. In general, it appears, that as the SoH degradation becomes more severe, the occurrence time of both the trough and plateau voltages is quicker and the difference between the plateau and trough voltage diminishes.

3.4. Water replenishment post-accelerated thermal ageing

The water lost during the accelerated thermal ageing of the cells in the previous section was estimated from the

Table 8
Cell capacities, original and post-accelerated thermal ageing weights

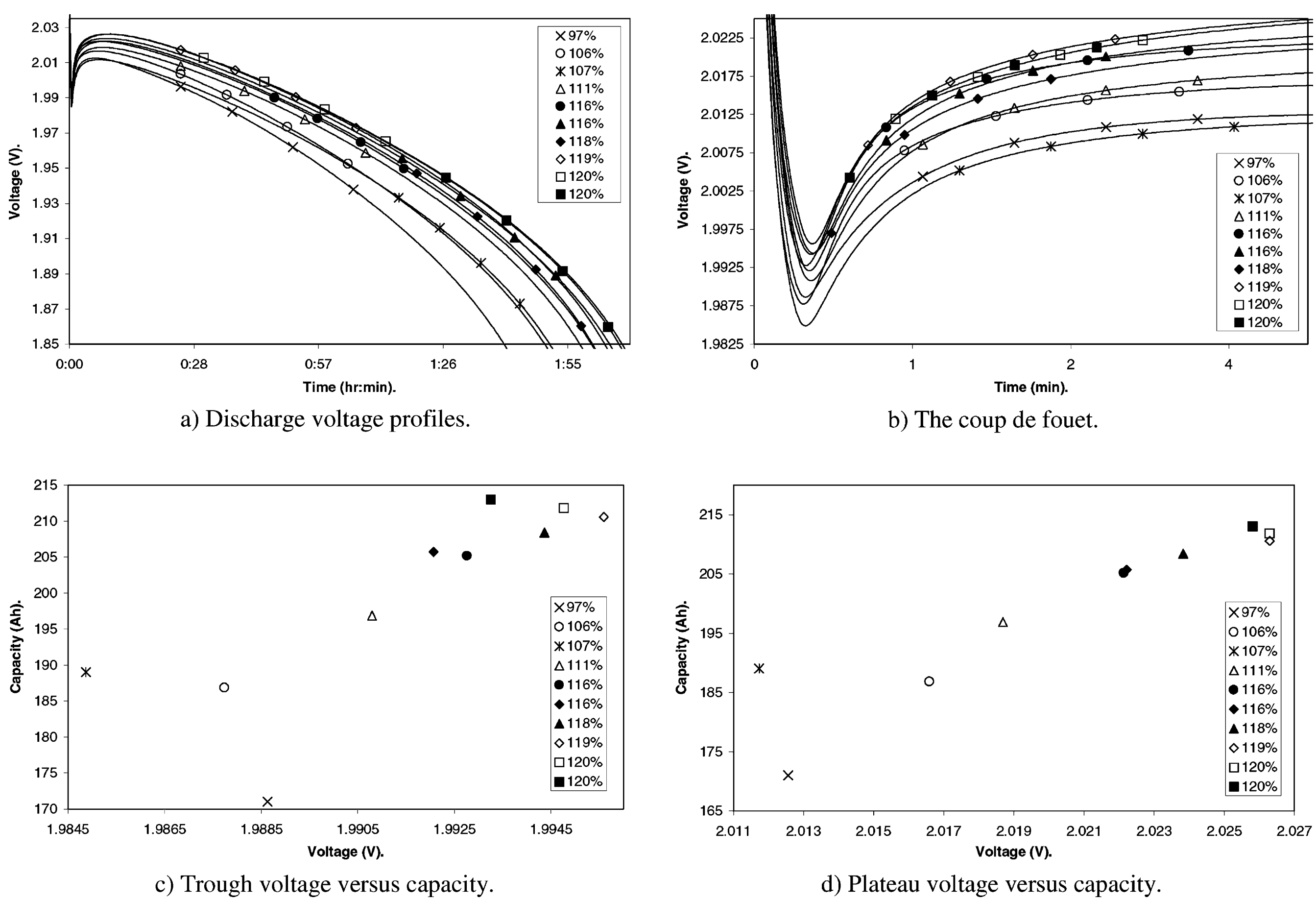
Discharge (% capacity)	Weight (g)		
	Original	Post-stress	Difference
123	18614.5	18616.5	−2
121	18688	18689.5	−1.5
109	18848.5	18687.5	161
102	18794	18646.5	147.5
64	18881	18644	237
64	18806	18577.5	228.5
45	18747.5	18554.5	193
30	18677.5	18501	176.5
21	18844.5	18554	290.5
10	18838	18544.5	293.5

Table 9
Time and charge released corresponding to occurrence of trough and plateau voltages and difference between trough and plateau voltages for discharge of cells with low SoH replenishment after accelerated thermal ageing

Discharge (% capacity)	Trough occurrence			Plateau occurrence			Plateau − trough difference (V)
	Time (s)	Charge released		Time (s)	Charge released		
		Ah	%		Ah	%	
120	30	0.829	0.389	416	11.512	5.404	0.033
120	28	0.773	0.365	544	15.061	7.110	0.032
119	32	0.899	0.427	497	14.001	6.649	0.031
118	32	0.887	0.425	475	13.187	6.327	0.029
116	30	0.843	0.410	480	13.520	6.572	0.030
116	28	0.784	0.382	399	11.215	5.466	0.029
111	31	0.831	0.422	429	11.909	6.048	0.028
107	28	0.785	0.415	379	10.663	5.641	0.027
106	27	0.756	0.405	371	10.426	5 580	0.029
97	28	0.785	0.459	331	9.309	5.443	0.024

weight lost as given in Table 8. The water was replaced and the cells were re-charged and then discharged. As a result of the addition of water, much of the cell capacity was recovered, i.e. to be between 97 and 120% of the rated capacity (see Table 9). The improvement in capacity is also clear from inspection of the discharge voltage versus time characteristics given in Fig. 12(a). A close up of the coup de fouet region is presented in Fig. 12(b) and effects a much greater consistency between the cells.

The relationship between the capacity due to the replenishment of water after the accelerated thermal ageing and the trough and plateau voltages is illustrated in Fig. 12(c) and (d), respectively. It can be seen here that, in both cases, the relationship is still close to linear, although not as consistent



a) Discharge voltage profiles.
b) The coup de fouet.
c) Trough voltage versus capacity.
d) Plateau voltage versus capacity.

Fig. 12. Influence SoH degradation due to water replenishment after accelerated thermal ageing.

Table 10
Sensitivity of trough and plateau voltage parameters to SoH degradation

Degradation mode	Capacity range		Trough voltage		Plateau voltage	
	Ah	%	Range (mV)	Sensitivity (mV/%)	Range (mV)	Sensitivity (mV/%)
New cells	199–206	113–116	2.6	0.72	2.8	0.80
Field ageing	161–208	91–117	31	1.19	30	1.15
Accelerated thermal ageing	18–217	10–121	96	0.86	121	1.09
Water replenishment after accelerated thermal ageing	171–213	97–120	11	0.48	15	0.65

as the relationships shown in Fig. 11(c) and (d) for the accelerated thermal ageing alone. Nevertheless, the majority of the coup de fouet parameters for the discharges closely follow the linear relationship with capacity, with only one or two not complying.

It can be seen in Table 9 that the occurrence times of the trough voltages for all coup de fouet are similar. There is more variation, however, with the occurrence times of the plateau voltages. The differences between the plateau and trough voltages, also given in Table 9, are now very similar, although a steady decrease which coincides with reduced capacity is apparent.

3.5. Sensitivity to SoH degradation

The sensitivity to various modes of SoH degradation (including that now cells), trough and plateau voltage coup de fouet parameters is given in Table 10. The sensitivity is presented in terms of mV per percentage capacity. This allows a valid comparison as the same type of cell (chemistry and size) and the same operating conditions have been used in all cases. It is clear that the greatest sensitivity corresponds to cells which suffer SoH degradation due to field ageing. That is, a change in battery capacity due to field ageing more clearly manifests itself in the coup de fouet.

4. Conclusion

The results of the 'black-box' analysis presented in this paper reveal the influence of a number of operational and battery conditions on the coup de fouet. The operating conditions considered are discharge rate ambient temperature, depth of previous discharge, charge duration and float voltage, while the battery conditions investigated include SoH degradation due to various forms of battery deterioration.

It is found that the occurrence times, as well as the magnitudes, of the coup de fouet trough and plateau voltages are inversely proportional to the discharge rate. By contrast, the magnitudes of the trough and plateau voltage parameters are directly proportional to ambient temperature, but the occurrence times are inversely proportional to ambient temperature. Thus, the magnitude of the coup de fouet parameters directly reflects the available capacity of the battery, with either parameter being low when capacity is low (corresponding to high discharge rate and/or low temperature), and vice versa.

A compound influence due to variations in the depth of the previous discharge is observed. Successive discharges to a depth of approximately 10% of rated capacity or less result in the occurrence of a second voltage dip. For consecutive discharges conducted to a depth of greater than 10%, the second dip does not occur. It is impossible, however, to decouple the influence of variations in charge duration from the influence of variations in discharge depth.

Variations in charge duration influence both the occurrence time and the magnitude of the trough and plateau voltages. Greater charge duration results in a lower coup de fouet parameter and a delayed occurrence time. The magnitude of the trough and plateau voltages is directly proportional to the float voltage within a float voltage boundary. The open-circuit voltage determines the lower limit of the boundary, while the upper boundary is found to be approximately 2.37 V (at an ambient temperature of 20 °C). The influence on occurrence time is subtle and more complex than that observed for the other operating conditions. It appears that the trough voltage occurs earlier for a higher float voltage, while the occurrence of the plateau is delayed.

Accelerated thermal ageing, water replenishment post-accelerated thermal ageing and field ageing are used to investigate the influence of SoH degradation on the coup de fouet. In all instances, it is found that the magnitudes of the coup de fouet parameters are directly proportional to the battery capacity. This is a significant result that highlights the potential for extracting battery SoH knowledge from the coup de fouet region. It is especially significant that the coup de fouet parameters corresponding to the discharge of cells suffering from SoH degradation through field operation exhibit a more dominant relationship with the resulting capacity.

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