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Aspects of nickel-cadmium cells in single cycle applications. II. Operational temperature effects

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The volumetric energy density picture is explored for nickel–cadmium cells in a single duty cycle application, over the operational temperature range − 30 to + 55° C. Results are presented showing that fresh, precycled cells easily attain the target specification (40–50 W h dm^{-3}) at temperatures at and above room temperature. Charge acceptance falls sharply at sub-zero temperatures however, and energy density reduces to critical levels below − 20° C. The charging characteristics and ability to achieve target performance at − 30° C depends markedly on cell origin and the permissibility of allowing some cell venting during the charge. The low temperature limitations can be overcome by means of low wattage heating coils on the cells. Internal temperatures of C and D/2 cells can be raised to 20° C within a few minutes by employing very modest temperature gradients and with heater volumes no greater than the manufacturers label and sleeve. Although the picture is optimistic for fresh precycled cells, major problems are anticipated with stored cells, particularly at temperature extremes, unless steps can be taken to prevent or erase storage effects.

1. Introduction

Applications exist whereby secondary batteries are used as primary reserve systems, activated by an electrical input [1]. The principal requirements of such applications are as follows: (a) a single duty cycle (possible maximum of two); (b) cells must be stored short-circuited for periods up to 10 years, at temperatures ranging between − 40 and + 70° C; (c) activation by charging must be completed within 1 hour; (d) energy density at the 24 hour discharge rate should be 40–50 W h dm^{-3}, 4–6·5 W h kg^{-1}; (e) up to 24 hour open-circuit stand period following charging; (f) operational temperatures (i.e. charge, stand and discharge) between − 30 and + 55° C; (g) cells must be sealed, venting during charge is permissible provided this does not include electrolyte mist or other corrosive materials.

Nickel–cadmium is the only couple likely to meet these specifications, at least in the immediate future. Published literature and manufacturers performance data affirms the suitability of fresh, unstored, commercial cells in ambients between 0° and + 40° C [1]. However, the performance of cells following extended periods of storage, and at the operational temperature extremes is less certain, particularly with regard to volumetric energy density. Storage effects are considered in the preceding paper [1], whilst this paper is concerned with defining fresh cell performance over the operational temperature range for which the following questions were posed.

For operation at sub-zero temperatures:

(a) What are the charge and discharge efficiencies, and hence derated energy densities, at − 30° C under the specified charge/discharge regime?

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(b) How is the current distributed between the charging and gassing reactions when cells vent during high rate overcharging at − 30° C?

(c) What are the external heater requirements and net benefits in uprating low temperature performance?

For high temperature operation:

(a) What are the charge and discharge efficiencies at + 55° C?

(b) What are the self discharge losses during stand and discharge at + 55° C?

(c) Does the specified charge regime at + 55° C create excessive cell temperatures?

1.1. *Low temperature effects*

Much information exists on the operational characteristics of nickel–cadmium cells at sub-zero temperatures, but different sources are often at variance with each other. This is not unexpected, considering the large number of influencing factors involved, namely temperatures and rates of charging and discharging, previous charge/discharge history, nature of charge (constant current, constant potential, pulsed, periodic reverse, etc.), origin and type of cell, etc. Quoted values of cell capacities from various sources ranged from 60% to below 30% of rated capacity, for a 24 hour discharge at − 30° C, following a 1 hour, 1·2 C charge at the same temperature. This pessimistic picture at low temperatures derives from the need to restrict the overcharge processes, hydrogen evolution on the negative and oxygen on the positive, which can produce rapid pressurization and ultimately, explosive failure of hermetically sealed cells if the charge is not terminated. With cells incorporating safety vents however, the picture is altered and related to the 'venting tolerance' of the cell. In multi-cycle applications, for which Ni/Cd cells are primarily designed, venting tolerance is low, since even one or two vents per cycle would result in premature cell failure through drying out, and serious imbalances can develop between the states of charge of the cell electrodes. A single cycle application however, allows consideration to be given to cell venting during charging, although understandably, no reliable quantitative information could be obtained on the benefits of such an operation, or the maximum amount of venting tolerated before subsequent discharge performance suffers serious limitations.

The problem of high rate charging at low temperatures can be overcome by using a heating coil to raise the cell temperature prior to charging. Although it is possible to calculate the required energy input, the more crucial factors are the temperature gradients existing, and the optimum power needed, to raise the cell internals, say to + 10° C or + 20° C, in the minimum time, whilst avoiding destructive temperatures at the cell periphery. Separator damage by hydrolysis and oxidation is the most likely cause of failure through overheating. In our experience, cells with polyamide separators have survived periods of 1 hour or so at temperatures between + 120° C and + 130° C, during rapid (1·2 C) charging. Polypropylene separators should be more capable of withstanding elevated temperatures, but it is probably inadvisable to allow case temperatures to exceed much more than 100° C, even with these materials.

1.2. *High temperature effects*

The charging of Ni/Cd cells at temperatures of + 55° C poses certain problems associated with the positive electrode. The nickel hydroxide electrode charge acceptance progressively decreases as the temperature increases, resulting in oxygen evolution earlier in the charge cycle. This reacts at the negative electrode, producing heat and a further temperature rise, and unless the charge is terminated, cells may suffer destructive thermal runaway. This is normally prevented by the use of thermal cut-outs; the cell voltage has a negative temperature coefficient and voltage cut-outs are, therefore, not used unless temperature compensated.

The reduced charge efficiency of nickel hydroxide positives naturally leads to decreased energy density. For example General Electric [3] quote the following values for a 0·1 C charge rate at 45° C:

(a) 55% charge acceptance for a 120% input.

(b) 70% charge acceptance for a 200% input.

(c) 80% charge acceptance for a 1000% input.

At 60° C the limiting capacity is 60% of nominal following a 1000%, 0·1 C input.

Charge acceptance of the positive electrode improves with increasing charge rate, reaching an optimum at about 2 C [5]. The problem then arises of the temperatures which might be generated with a 2 C overcharge.

Once charged, the application calls for an open-circuit stand of up to 24 hours, before the 24 hour rate discharge. During this period the cell will be subject to self-discharge of the positive electrode at elevated temperatures. Self-discharge rates vary according to manufacturer and cell type, with quoted values ranging between 5% and 30% losses per day at + 55° C. The processes would be doubly important if self-discharge also occured during the 24 hour discharge period, unless polarization on load is sufficient to discourage these parasitic effects.

In the worst extreme, the problems of high temperature operation for this application could be more acute than the sub-zero ones, since the latter may be overcome by cell heating, whereas cell cooling from + 55° C is a less feasible option.

2. Experimental

2.1. *Low temperature experimental*

2.1.1. Low temperature charge–discharge tests: 5 C-size sintered electrode Ni/Cd cells, of nominal capacity 2 A h, from each of three manufacturers were charged from a constant current d.c. power supply, at − 30° C, 1·2 C rate, for 1 hour. Charging was carried out under ethyl alcohol in a 1 litre burette and the volumes of vented gases measured. Cell voltage was also monitored during charging.

Charged cells were discharged at the 24 hour rate through 15 Ω resistors to a 1 V cut-off level. Three of each manufacturer type were discharged at − 30° C and two at + 20° C. Discharge capacities (Ah) were calculated from the mean discharge voltage, load resistance and time to 1 V cut-off.

To eliminate any disparate storage effects, the cells were given a preconditioning cycle at + 20° C under the same regime.

2.1.2. Heating of cells from − 30° C to + 20° C: For a 2 A h nominal capacity, there is a choice of physical cell sizes, namely the C and D/2 types. Whilst the electrical capacity is the same, they have different aspect ratios (height to diameter) which will affect the temperature gradients across the cells. Both cells were therefore, used in these studies.

Labels were removed from C and D/2 cells of manufacturer 2 and insulated, 37 SWG copper wire was used to wind a heater coil onto the outer casings. A layer of self-adhesive, woven, glass-filled, silicone electrical tape (about 0·2 mm thick) was used to constrain the coils and provided a small amount of thermal insulation. The overall volume of the heater in each case was about the same as the manufacturer's label and could therefore, be neglected in any subsequent estimations of volumetric energy density.

Thermocouples were sited at points 1, 2, 3, 4 and 5 on each cell as shown in Fig. 4.

Constant d.c. current was used to heat the coil and, as a result, the power input changed slightly as the coil temperature increased.

The time variation of each thermocouple output was logged at different heater power inputs between 5 and 50 W.

2.2. *High temperature experimental*

Four, sintered electrode, C-size cells, of nominal 2 A h capacity, from each of 2 manufacturers (manufacturers 1 and 3 of the low temperature work) were subjected to the following sequence of charge/discharge cycles:

(a) First conditioning cycle; charged at 1·2 C from a constant current power supply for 1 h at + 20° C. Discharged at 0·2 C (3 Ω load) at + 20° C to 1 V cut-off.

(b) First high temperature cycle; charged at 1·2 C for 1 h at + 55° C. One hour stand at + 55° C, then discharged at 24 hour rate (15 Ω load) to 1 V cut-off.

(c) Second conditioning cycle; cells cycled as first conditioning cycle.

(d) Second high temperature cycle; cells cycled as first high temperature cycle except that a 24 h stand at + 55° C was used instead of the 1 h above.

Cell temperatures were monitored throughout the charge periods by means of thermocouples attached to the cases.

3. Results

3.1. *Low temperature results*

3.1.1. Low temperature charge–discharge tests. Representative gas evolution and voltage character-

Table 1. Charge–discharge data for C-size cells of different manufacture [all cells charged at 1·2 C (2·4 A) for 1 hour at — 30° C, discharged 24 hour rate (15 Ω resistor) to 1 V cut-off at the indicated temperature]

Manufacturer	*Cell number*	*Discharge temperature* (° C)	*Charge in to venting* (A h)	*Total gas vented* (cm^3 at NTP)	*Total gas vented assuming all H_2* (A h)	*Total charge returned* (A h)	*Mean discharge voltage* (V)	*Energy density* (W h dm^{-3})
1	1	— 30	0·8	289	0·7	0·7	1·23	39
1	2	— 30	0·6	635	1·5	0·6	1·24	34
1	3	— 30	0·5	860	2·1	0·6	1·23	34
1	4	+ 20	0·8	275	0·7	1·0	1·19	54
1	5	+ 20	2·4	0	0	1·0	1·25	57
2	1	— 30	0·24	730	1·75	1·15	1·15	60
2	2	— 30	0·24	764	1·83	0·93	1·16	49
2	3	— 30	0·24	809	1·94	0·91	1·19	49
2	4	+ 20	0·24	809	1·94	1·39	1·14	72
2	5	+ 20	0·12	871	2·09	1·38	1·07	67
3	1	— 30	0·36	618	1·48	1·09	1·28	64
3	2	— 30	0·36	674	1·61	0·98	1·30	58
3	3	— 30	0·48	663	1·59	1·24	1·33	76
3	4	+ 20	0·20	629	1·51	1·46	1·23	82
3	5	+ 20	0·24	725	1·73	1·49	1·29	87

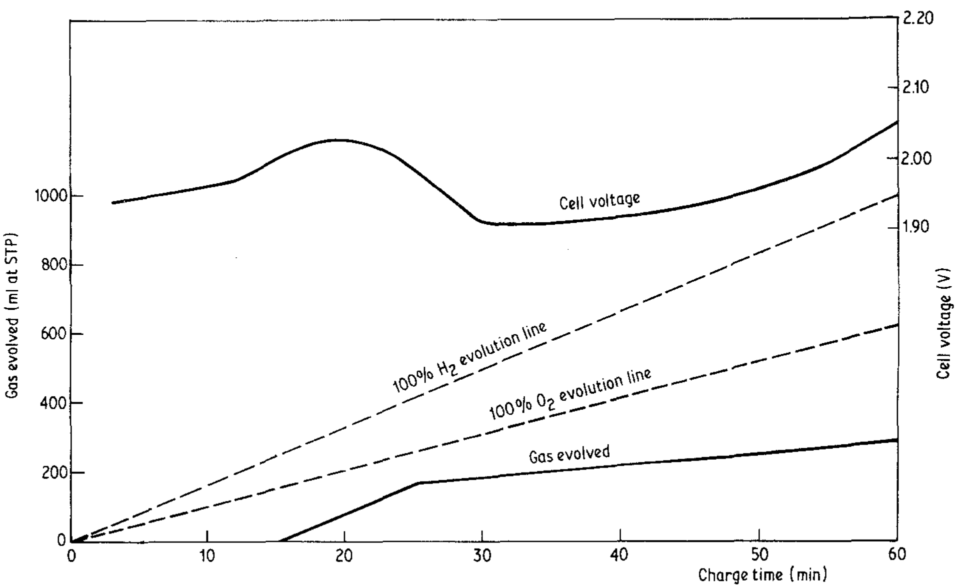

Fig. 1. Typical gas evolution and voltage characteristics of manufacturer 1 C-cells during — 30° C, 1·2 C charging.

istics during charging of the three sets of different manufacturers' cells are shown in Figs. 1–3. Charge–discharge data for all cells is summarized in Table 1.

There was a marked difference in charge behaviour between manufacturer 1 cells and the other two sets of cells. The latter vented gases after accepting only about 10–20% charge input and were evidently limited principally by the negative electrode. Thus the characteristic voltage depression normally exhibited by sealed cells under overcharge, and caused by heating and depolarization effects from oxygen evolving at the positive and recombining at the negative cadmium electrode [4], was virtually absent with these cells. The gas venting rates were much too high to be caused solely by slow oxygen recombination at the negative and the vented gases must have con-

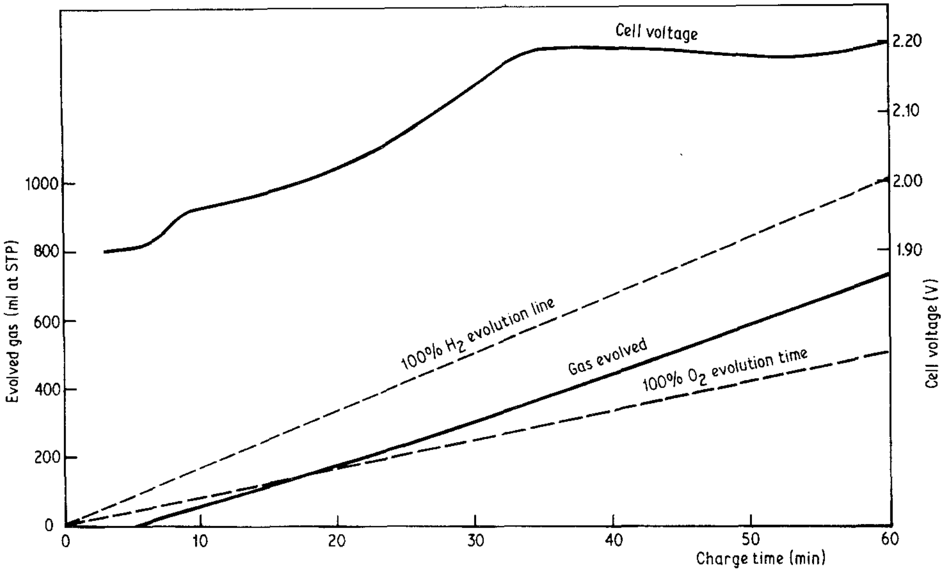

Fig. 2. Typical gas evolution and voltage characteristics of manufacturer 2 C-cells during — 30° C, 1·2 C charging.

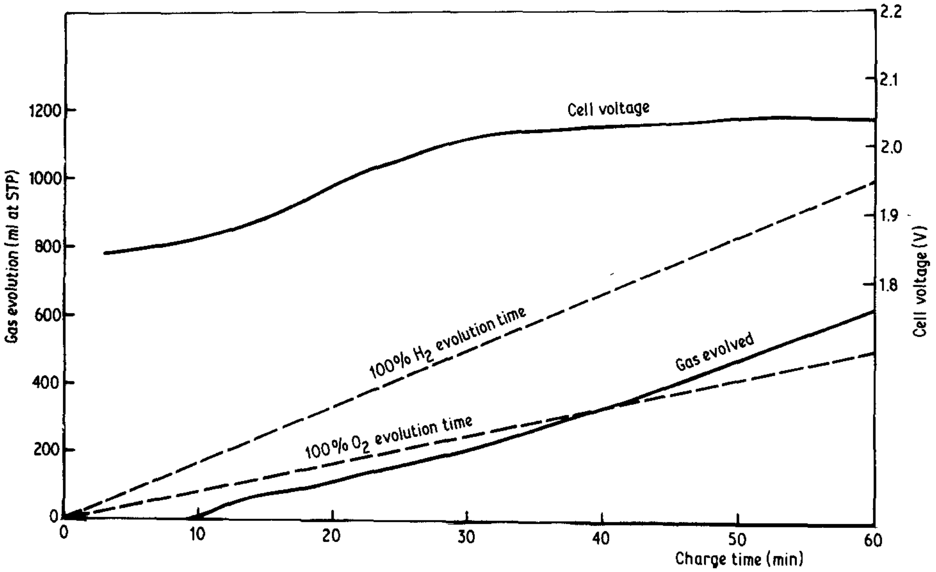

Fig. 3. Typical gas evolution and voltage characteristics of manufacturer 3 C-cells during — 30° C, 1·2 C charging.

tained a high proportion of hydrogen which does not recombine to any significant extent in sealed Ni/Cd cells.

In contrast, manufacturer 1 cells did not vent until about 20–30% charge had been accepted and the subsequent amounts of gas were much more variable from cell to cell. All except cell 3 exhibited a sharp voltage depression, indicating the onset of oxygen recombination at the negative electrode. In most cases, this voltage depression virtually coincided with the onset of venting (see Fig. 1). Cell 3 commenced venting after about 20% charge input and exhibited an ill-defined voltage depression after about 70% charge input. Cell 5 was accidentally short-circuited before testing and did not vent any gas during the charge period. It is possible that this rapid discharge preceding the cell 5 test, resulted in morphological changes of the cadmium hydroxide in the negative which imparted a higher charge acceptance to this electrode [2]. The behaviour of manufacturer 1 cells suggests that charge acceptance is governed by processes occuring at both electrodes to varying extents, ranging from complete positive control in cell 5 to almost complete negative control in cell 3.

From a purely practical standpoint, if the cells were charged at — 30° C until they vented, and then the charge terminated, the volumetric energy density at — 30° C of manufacturer 1 cells would be greater than the other two sets of cells, but all would fall below the target performance. If venting is permitted however, the cells of manufacturers 2 and 3 would continue to accept some charge and achieve the minimum specified volumetric energy density of 40–50 W h dm^{-3}, whereas the cells of manufacturer 1 would not exhibit any significant electrode charging after the venting point and would remain below specification.

Volumetric energy densities of all 3 groups of cells during the conditioning cycle at + 20° C were about 120 W h dm^{-3}. Comparison of this figure with energy density values quoted in Table 1 enables the following estimates to be made of energy losses when operating at — 30° C, relative to + 20° C:

(a) Total energy losses (difference between mean energy density values of cells 1, 2 and 3 in Table 1 and the + 20° C value): manufacturer 1, 66%; manufacturer 2, 51%; manufacturer 3, 40%.

(b) Energy losses due to charging at — 30° C, (difference between mean energy density values of cells 4 and 5 in Table 1 and the + 20° C value): manufacturer 1, 50%; manufacturer 2, 37%; manufacturer 3, 24%.

(c) Energy losses due to discharging at — 30° C (difference between mean values of cells 1, 2, 3 and those of cells 4 and 5 in Table 1): manufacturer 1, 16%; manufacturer 2, 14%; manufacturer 3, 16%.

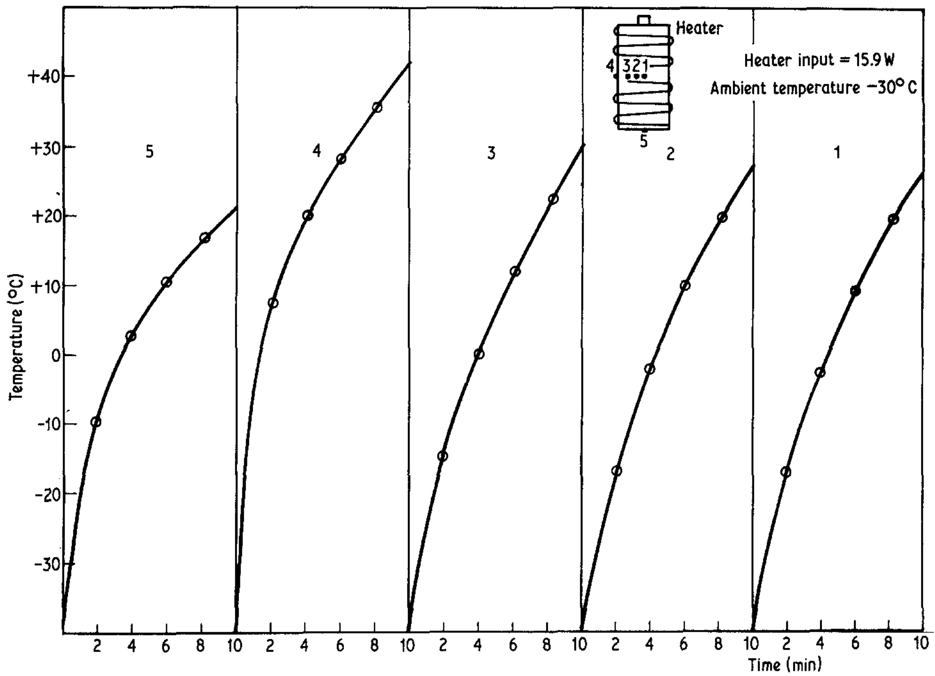

Fig. 4. Temperature profile of manufacturer 2 C-cell.

3.1.2. Cell heating tests from — 30° C. The temperature profiles at five locations for 16 and 21 W heaters, wound on C and D/2 cells respectively, are shown in Figs. 4 and 5. The times to heat C and D/2 cells from — 30° C to + 20° C are shown as functions of heater power in Fig. 6. The results show that cell heating to + 20° C is possible within 5–10 min using a moderate, 20 W heater power, without producing excessively high temperatures at the cell case. The highest temperature recorded

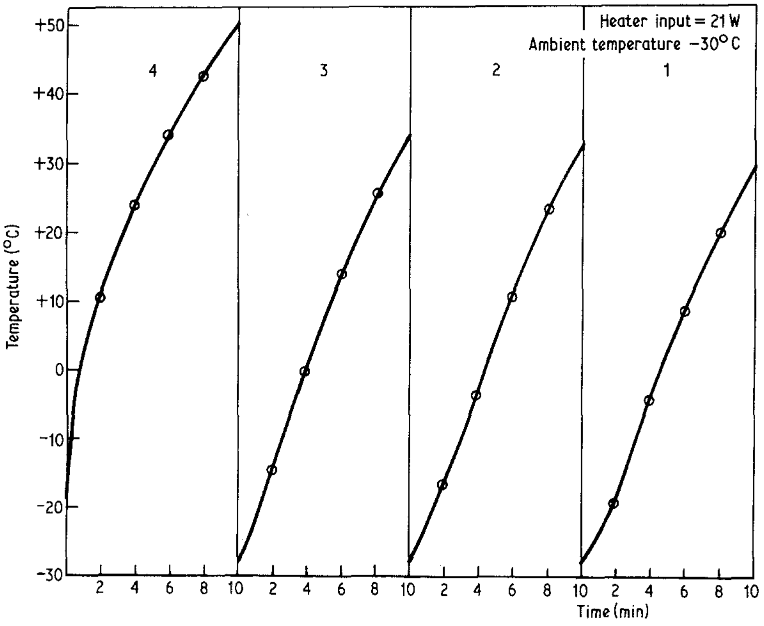

Fig. 5. Temperature profile of manufacturer 2 D/2-cell.

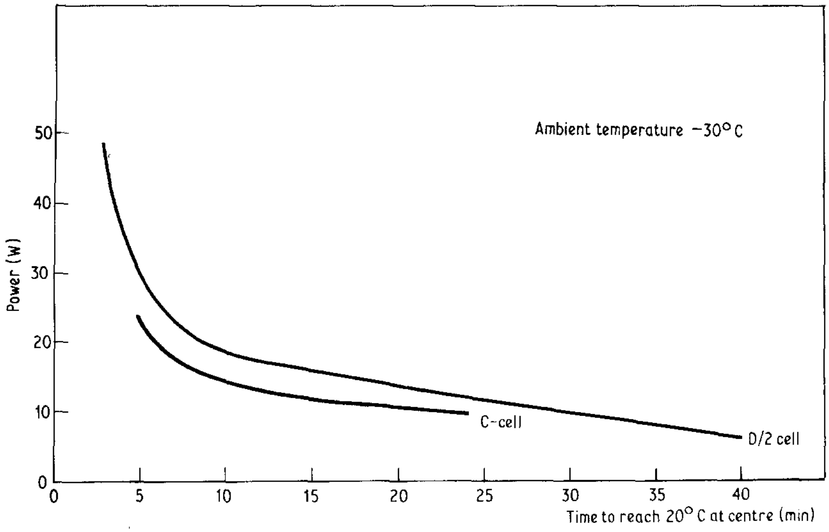

Fig. 6. Power versus time to 20° C for manufacturer 2 D/2- and C-cells.

with this heater power was + 50° C on the D/2 cell, at the case periphery (Fig. 5).

3.2. *High temperature results*

The results of the high temperature tests are given in Table 2 which show a reduction in volumetric energy density, relative to rated values at + 20° C, of about 17% for the + 55° C, 24 hour stand cycle and 3% for the + 55° C, 1 hour stand cycle.

The lowest recorded value of energy density at + 55° C was 85 W h dm^{-3} on a 24 hour stand cycle, which is well within the target specification.

The range of case temperatures, measured during charging at + 55° C, are shown in Fig. 7. Temperatures were within acceptable limits with charge inputs up to 120% of nominal at the 1·2 C rate, in + 55° C ambients, but greater inputs would soon result in dangerously high cell temperatures.

Table 2. Discharge data for C-size cells of different manufacture

	Manufacturer 1				*Manufacturer 3*			
	Cell 1	*Cell 2*	*Cell 3*	*Cell 4*	*Cell 1*	*Cell 2*	*Cell 3*	*Cell 4*
1st condition cycle								
discharge capacity (A h)	1·95	2·03	2·02	1·96	1·84	2·10	2·00	1·93
mean cell voltage (V)	1·26	1·26	1·26	1·26	1·26	1·26	1·26	1·25
energy density (W h dm^{-3})	112	116	116	112	105	120	115	110
1st high temperature cycle								
discharge capacity (A h)	1·81	1·97	1·95	2·01	1·77	2·05	1·78	1·75
mean cell voltage (V)	1·24	1·27	1·25	1·27	1·24	1·26	1·25	1·25
energy density (W h dm^{-3})	102	114	111	116	100	117	101	99
2nd condition cycle								
discharge capacity (A h)	1·90	1·97	1·97	1·97	2·01	2·16	2·10	2·01
mean cell voltage (V)	1·27	1·27	1·27	1·27	1·25	1·26	1·26	1·25
energy density (W h dm^{-3})	110	114	114	114	114	124	120	114
2nd high temperature cycle								
discharge capacity (A h)	1·73	1·72	1·80	1·60	1·60	1·74	1·49	1·51
mean cell voltage (V)	1·22	1·21	1·23	1·21	1·23	1·25	1·25	1·24
energy density (W h dm^{-3})	96	95	101	88	89	99	85	85

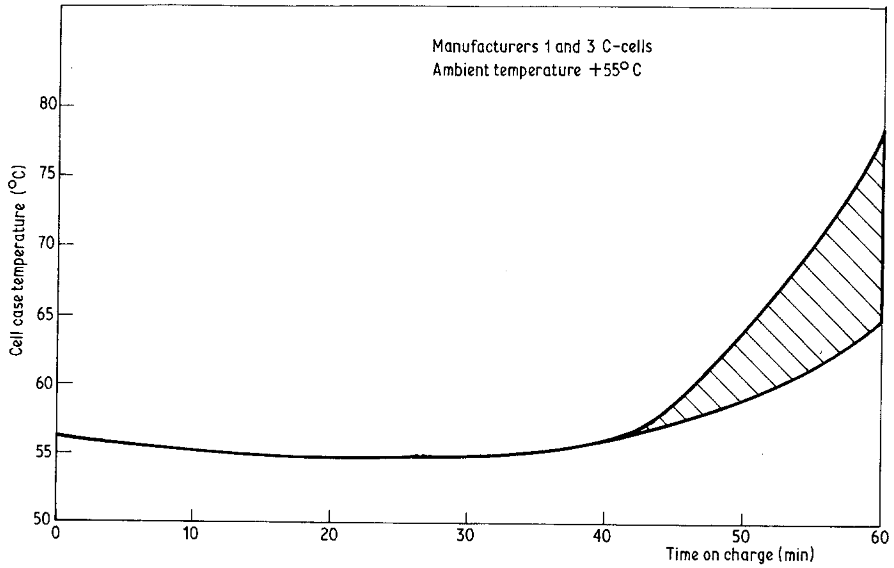

Fig. 7. Temperature of cell case on + 55° C, 1·2 C charge.

4. Conclusions

The overall volumetric energy density picture for nickel–cadmium cells in the single duty cycle application, over the temperature range — 30° C to + 55° C, is shown in Fig. 8. The data for stored cells was estimated from the relationship derived in the previous paper [1]. All data applied to a 1·2 C, 1 hour charge, followed by a 24 hour rate discharge to 1 V cut-off, at the temperature indicated. Two problem areas exist:

(a) low temperature charging below — 20° C.
(b) storage effects.

The low temperature problem originates principally from decreased charge acceptance at either the positive or negative electrode, depending on origin and previous charge/discharge history of the cell. At — 30° C cells attain an overcharge condition after only about 10–20% nominal capacity input, manifested by a steep rise in cell voltage and venting of significant amounts of gas from the safety valve. In the single duty cycle

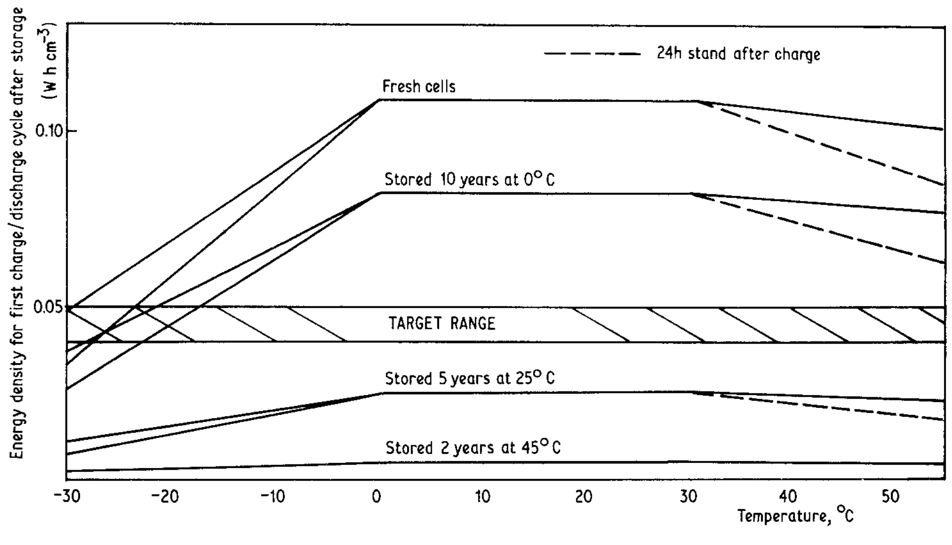

Fig. 8. Volumetric energy density picture for nickel–cadmium cells in a single duty cycle application.

application, charging may be permitted beyond this point with varying benefits, again depending on cell origin and previous history.

A simple, low power heater can be used to boost performance of cells at − 30° C to the + 20° C levels, provided the extra power lines can be accommodated.

Storage effects present a more acute problem. Refrigeration below 0° C would inhibit storage degradation to within reasonable limits but is not a practical option for this particular application.

Other measures to either prevent or erase storage effects, and to boost low temperature performance, are under investigation and will be considered in following publications.

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