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Rechargeable alkaline manganese dioxide cells. A test report

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Abstract

The rechargeable alkaline MnO_2 (RAM) system has now been commercially available for several years. The Canadian Department of National Defence is interested in determining if the low cost RAM system is technically capable of replacing existing cells and batteries now in use. A preliminary study identified sufficient candidate batteries in use within the Department whose performance requirements compared favourably with RAM manufacturers' claims. Further study was warranted. Replacement cost savings could be significant. A study is now in progress that is aimed at determining how well the RAM technology actually performs. This paper presents test results that illustrate how RAM cells compare to primary alkaline cells and nickel/cadmium. The majority of the work is focused on the 'AA' size products from Rayovac and Pure Energy: tests were also conducted on Rayovac 'D' cells.

Keywords: Zinc anode secondary batteries; Performance

1. Introduction

Could RAM technology play a major role in the Canadian Forces (C.F.) battery management plan? That is the question to be answered in this current study of RAM technology. There are a number of possible roles being considered. The C.F. procure a large number of primary alkalines in much the same way that any large organisation might in order to power desktop electronics and other portable equipment. The C.F. also consume many batteries in the field, particularly in training and exercises. The requirements for training and exercise batteries are somewhat less than those of operational packs, particularly in terms of the temperature of operation. For example, many exercises occur in the warmer weather months where nickel/cadmium and alkalines are often used in place of lithium batteries.

The US Army has identified the need for a rechargeable training and exercise battery that lasts for approximately 100 cycles and powers equipment for approximately 8 h a day. This new thinking opens the door to RAM technology. Studies such as these are being conducted to identify if low cost RAM batteries could meet this requirement.

The high cost of lithium batteries, the move away from the practice of procuring to military specifications and the constant pressure to reduce costs were factors motivating this assessment of RAM technology.

This report contains some data that are similar to data published by manufacturers of RAM cells. The results presented here were generated independently of manufacturers.

The overall assessment of RAM technologies was divided into three phases. The first phase was a theoretical cost benefit analysis of adopting RAM technology into the C.F. Primary alkaline, nickel/cadmium and other battery technology in use in the C.F. that would theoretically be candidates for replacement with RAM technology were identified. These candidates had characteristics that were comparable to literature available at the time describing RAM cell performance.

Interviews with the manufacturers of RAM products were also helpful. Projected RAM technology costs were substituted for the C.F. battery procurements where warranted by claimed RAM performance. Conservative factors were applied for cycle life and for the costs of adopting the new technology such as new chargers.

The conclusion of this first phase: on a theoretical basis, adoption of RAM technology could potentially save the C.F. significant money on an annual basis.

The technical assessment of RAM technology was therefore the next logical step. How well does RAM actually work? How robust is it compared with the technologies it could possibly replace? Numbers based upon experimental tests needed to be generated. It is this second phase of the study that is reported here. The cell level experiments are nearly complete and battery level experiments are underway.

This paper will be limited to the cell level work. Although the battery experiments are not reported here, it should be noted that they may indeed be the application where RAM technology plays its greatest role in reducing costs in future.

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The literature has been reporting the potential of RAM in battery packs for many years [1].

Upon completion of the technical assessment of RAM, the cost benefit analysis will be repeated substituting the experimentally derived values for performance. A final analysis of the benefits of RAM in the C.F. will be made, influenced by all that was learned during the second phase.

2. Experimental

Experiments were conducted on primary alkaline and nickel/cadmium cells for comparison with RAM products. The scope of the study did not allow for more than one make of nickel/cadmium 'AA' or primary alkaline 'AA' and 'D' cell to be studied. The models chosen were selected because of the reputation of their makers for high quality within the industry coupled with their availability, not as an endorsement of the particular brands.

The primary alkalines studied were Panasonic models AM3X AA and AM1X D cells.

The nickel/cadmium cells were Panasonic model P-60AA; their standard 600 mAh AA size.

Rayovac Renewal™ AA model 715 (Lot 51019 manufactured 19 Oct. 1995) and Rayovac Renewal™ D model 713 (Lot 51109 manufactured 9 Nov. 1995) and Pure Energy™ AA model 30003 (no lot information provided) were studied.

All cells were obtained directly from the manufacturers in the Oct./Nov. 1995 period. For purposes of brevity the RAM cells will be referred to as Rayovac AA, Rayovac D and Pure Energy AA in this text. There is no Pure Energy equivalent to the Rayovac D cell therefore no D cell comparison was possible.

Based upon the results of the survey of the C.F. use of batteries, only AA and D cell experiments were conducted. AA cell experiments were of greater interest. All cell level experiments were conducted in triplicate. Experiments were conducted in controlled temperature chambers with ± 1°C control or better with the following exceptions. Nickel/cadmium cells were always charged at room temperature, $C/10$ (60 mA) for 16 h. Some RAM charging was performed at room temperature in commercial RAM chargers. Both Rayovac Renewal PS1 and PS2 and Pure Energy CS4 chargers were employed as indicated. In other experiments, RAM cells were cycled on an automated cycler set to limit voltage to 1.65 per cell and current to 250 mA for AA cells, 400 mA for D cells. The automated cycler had the advantage of allowing cells to be charged at the required experimental temperature.

For RAM cells, in all cases, charging was limited to 1.65 V and discharges were cut off at 0.9 V.

Primary alkalines were discharged to 0.5 V and capacities were calculated to 0.9 V.

Nickel/cadmium cells were discharged to 1.0 V.

AA cells of all types were discharged on 3.9 ohm loads except for a study of the effect of rate of discharge where 39 and 390 ohm loads were employed.

Likewise, D cells were discharged on 2.2 ohm loads except for experiments conducted with 22 and 220 ohm. Loads were calibrated by passing 100.0 mA through the apparatus from the cell holders and measuring the d.c. voltage. Ohm's Law was then applied to determine the exact load for each experiment. By this means, loads were calibrated and characterised to within $\pm 1\%$.

Storage tests consisted of placing the cells in a temperature chamber for the prescribed period of time then, after suitable equilibration, cycling the cells at 20°C for 30 cycles.

Two methods of charging RAM cells were evaluated: pulse charging with commercially available chargers and d.c. taper charging with an automated cycler.

For AA cells, experiments conducted on an automated cycler charged the cells with a constant current to a voltage limit of 1.65. Once the upper voltage limit was reached, the d.c. current would taper off. Charging was terminated after 12 h. Two constant currents were compared: 250 and 400 mA.

For D cells, the cycler was limited to 400 mA, 1.65 V per cell and charging was terminated after 20 h.

3. Discussion of results

3.1. The effect of chargers and charging method

Pulse charging was accomplished using the Rayovac Renewal PS1 and PS2 chargers and the Pure Energy CS4 charger. The PS1 charges only AA and AAA cells and charges the cells at lower currents than the larger PS2 charger. The PS2 charger will charge AAA, AA, C and D cells. The PS1 and PS2 chargers were compared. No significant differences in cell performance were found. For convenience, the PS2 charger was adopted as the standard charger for Rayovac cells. The Pure Energy CS4 charger charges AA cells only. Also, a d.c. taper charge method employed by the automated cycler was compared with the commercial chargers. Finally, Pure Energy cells were charged in the Rayovac chargers and vice versa.

Both Rayovac and Pure Energy chargers use LEDs to indicate charge completion. The Rayovac PS2 charger indicates when each individual cell is charged. The Pure Energy CS4 charger has a single LED that indicates when all cells in the charger are charged. It was determined that removing cells from either charger when the LED indicated charge completion resulted in delivered capacities that were not as reproducible as charging the cells for a fixed time. This effect was not drastic, but indicates that the chargers do not cease to charge when the LED indicates complete charge.

Fig. 1 illustrates that there was little difference in delivered capacity per cycle, regardless of the charging method. The

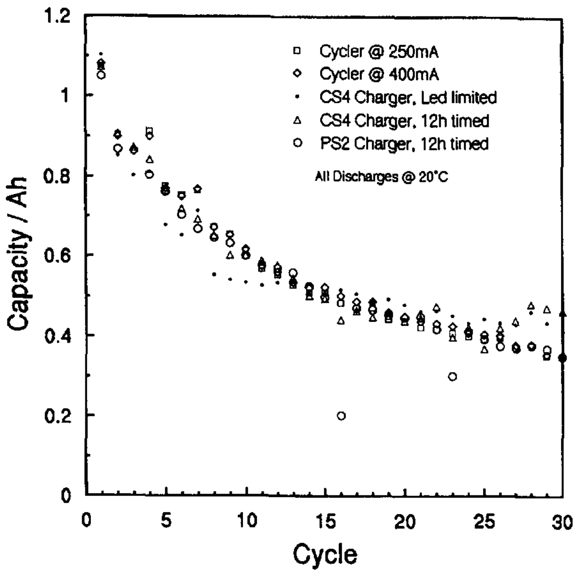

Fig. 1. The delivered capacity after charging Pure Energy AA cells by five different methods. All discharges: continuous 3.9 ohm, 20°C.

results illustrated are for Pure Energy AA cells. A similar result was obtained for Rayovac AA cells.

3.2. Capacity comparisons

To determine a basis for capacity comparison is difficult when comparing three different technologies. A standard load for each format (3.9 ohm for AA, 2.2 ohm for D) was adopted to keep the scope of the experiments reasonable.

A look at the bars marked 1 in Fig. 2 show the first cycle capacities of Pure Energy AA, Rayovac AA, primary alkaline AA, and nickel/cadmium AA at 20°C on 3.9 ohm. The capacity obtained on the first cycle of a RAM cell is lower than primary alkalines due to formulation changes required for recharging tolerance [2]. RAM cells are clearly superior to nickel/cadmium cells for the first cycle at 20°C. At lower rates of discharge, RAM cell capacity per cycle increases, as discussed later.

One explanation for the differences identified between Rayovac and Pure Energy cell capacities could possibly be as simple as batch to batch variation. On the other hand, it might also have been due to formulation differences between the Rayovac and Pure Energy. No definitive explanation of the results was determined.

The moderate 3.9 ohm continuous load experiments produced lower capacities than would be expected from intermittent drain on the same load: a characteristic of the alkaline system [3].

How fair is it to make 30-cycle comparisons against nickel/cadmium that could easily do 200 cycles or more? A clever battery design could possibly take good advantage of the superior capacities in the initial cycles of RAM cells versus nickel/cadmium.

Consider that a battery pack assembled from nickel/cadmium AA (or other size) cells could be replaced by a pack

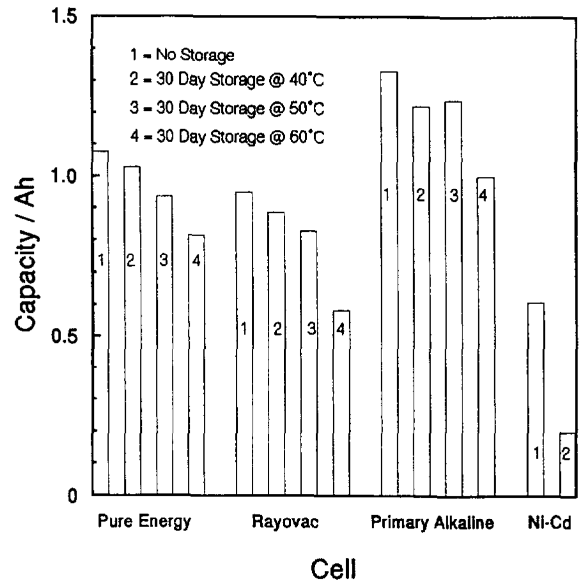

Fig. 2. First cycle capacity of AA cells: continuous 3.9 ohm load, 20°C. Bars labelled 1 are nominal capacity immediately after charge. Bars labelled 2, 3 and 4 show the deteriorations due to charged stands at elevated temperatures.

made up from multiple strings of RAM AA cells in the same form factor. If the application demanded a low or moderate rate of discharge or a suitable pulse discharge regime, the RAM pack might only have to discharge 30% of its first cycle capacity to compete with the 100% discharge of the nickel/cadmium pack. Recharging after only partially discharging the RAM pack would result in an extended cycle life of the RAM pack, possibly the 100 cycles targeted for useful field service life identified by the US Army [4]. The RAM pack would meet the application at a slightly higher average voltage, and cost less to build. It would also save on the disposal cost of the nickel/cadmium, a significant life-cycle cost saving. Could this be a low cost training and exercise battery for military applications?

The single cell performance cited here does not prove this scenario would work. Battery tests are therefore underway to characterise the cycle life enhancement of partial discharges of RAM technology. Preliminary results are encouraging.

3.3. The effect of storage

Two distinctly different storage tests were undertaken. The first, and simpler, was to set aside cells at room temperature for periods of six and twelve months and compare their resulting capacities. The charge retention of RAM is vastly superior to nickel/cadmium. Nickel/cadmium cells are well documented as being particularly poor at holding charge [3]. As a result, standard operating procedure with nickel/cadmium requires that the batteries be charged immediately before use. RAM technology could become attractive for many field applications where charging before use is costly, inconvenient or impossible.

After six months of storage at 20°C, both the Rayovac and Pure Energy AA cells increased in capacity (30-cycle cumu-

Table 1
Effect of high temperature storage: 30-cycle cumulative Ah capacity

Type/storage time (days)	Store temp./cumulative capacity (Ah)		
	40°C	50°C	60°C
Pure Energy AA			
30	17.4	17.5	16.6
60	17.9	17.4	16.2
90	17.8	16.3	15.1
Rayovac AA			
30	14.6	15.2	11.5
60	15.2	11.8	8.1
90	13.9	13.3	8.1
Rayovac D			
30	68.3	65.1	14.5 [a]
60	68.1	37.3	16.5 [a]
90	70.8 [b]	38.9	7.4 [a]

[a] Single cell result. Two out of three cells failed.
[b] Suspect value: possibly affected by problems associated with cycling equipment used during these experiments.

lative) by 2% over their 'as received' capacity at 20°C. The Rayovac D cells had decreased 15%. The twelve month storage tests are still in progress.

The second storage test evaluated the RAM products' ability to be stored at elevated temperatures. The experimental matrix consisted of three storage temperatures (40, 50 and 60°C) and three storage intervals (30, 60 and 90 days).

Subsequently, after removal from storage, 30 cycles at 20°C produced the cumulative capacities (average of three cells) presented in Table 1. The Pure Energy AA cells demonstrated good tolerance for all storage conditions. Storage at 40°C appeared to improve the capacity of the cells slightly over time. The higher temperatures had a small detrimental effect. The Rayovac AA cells did not behave the same way as the Pure Energy cells. After storage at 40°C they lost some capacity. Higher temperatures induced greater losses in capacity in the Rayovac AA than the Pure Energy AA. The Rayovac D cell was tolerant of 40°C storage. Storage at 50°C caused a drastic variation in performance (8.3, 45.8 and 62.7 Ah, respectively, for the three cells held for 90 days at 50°C) and some leaking. At 60°C, most of the cells failed completely. Survivors were drastically reduced in capacity.

Fig. 2 shows first cycle capacities of AA products after 30 days storage at various temperatures. Pure Energy and Rayovac AA cells behaved in a similar fashion to the Panasonic primary alkaline cell. The nickel/cadmium results are only comparable at 40°C storage. Whereas all the RAM and primary alkaline cells lost only a few percent after 30 days storage at 40°C, the nickel/cadmium cells lost two thirds of their charge. RAM cells, like the primary alkaline cells, were clearly superior to nickel/cadmium after storage at elevated temperatures prior to cycling.

3.4. *The effect of temperature*

Two approaches to the study of RAM performance at low temperatures were undertaken. In one set of experiments, cells were time-charged in their commercial chargers at room temperature, then discharged at the experimental temperature after equilibration. A summary of the results is presented in Table 2. Experiments were conducted at 20, 0, −10 and −15°C. The 20, 0 and −15°C results are complete. RAM cells behaved in a similar fashion to the primary alkaline, suffering with decreasing temperature. The Rayovac AA outperformed the Pure Energy at −15°C, otherwise Pure Energy was slightly better than the Rayovac at 0 and 20°C. The nickel/cadmium AA cells performed well at all conditions.

The Rayovac D cells delivered 4.5, 1.8 and 0.6 Ah on first cycle at 20, 0 and −15°C, respectively. D cells discharged at 20°C averaged 70.6 Ah cumulative capacity after 30 cycles. All three D cells discharged at 0°C failed at 28 cycles and delivered an average of 22.9 Ah before failure. One of the three D cells failed on charge after 17 cycles at −15°C. The other two D cells tested at −15°C delivered an average of 21.9 Ah but one cell was significantly lower in capacity than the other.

Charging and discharging (automated cycling) at the experimental temperature was the second approach. Once again, experiments were conducted at 20, 0, −10 and −15°C, however only the 20 and −15°C results are complete. The results are summarised in Table 3.

3.5. *The effect of rate of discharge*

Cells were charged in their respective commercial chargers (the Rayovac PS2 and Pure Energy CS4) at room temperature and discharged at 20°C. For AA cells, the three discharge conditions were set by loads of 3.9 (nominal), 39 (medium) and 390 (low) ohm. For D cells 2.2, 22 and 220 ohm loads were employed.

Table 2
Delivered capacity in Ah during low temperature discharges of AA cells following a charge at room temperature

Temp (°C)	Primary alkaline	First cycle (Ah)			Cumulative Ah over 30 cycles		
		Rayovac	Pure Energy	Ni/Cd	Rayovac	Pure Energy	Ni/Cd
20	1.3	0.95	1.1	0.61	14.3	17.1	18
0	0.6	0.37	0.49	0.59	6.7	7.2	17
−15	0.15	0.17	0.13	0.56	4.3	3.7	14

Table 3
Delivered capacity (Ah) on cycling (charging and discharging) of AA and D cells at 20 and −15°C

Temp. (°C)	First cycle (Ah)			Cumulative Ah over 30 cycles		
	Rayovac AA	Pure Energy AA	Rayovac D	Rayovac AA	Pure Energy AA	Rayovac D
20	0.95	1.1	4.4	16.1	16.9	70.2
−15	0.16	0.14	0.71	3.9	3.3	22.3

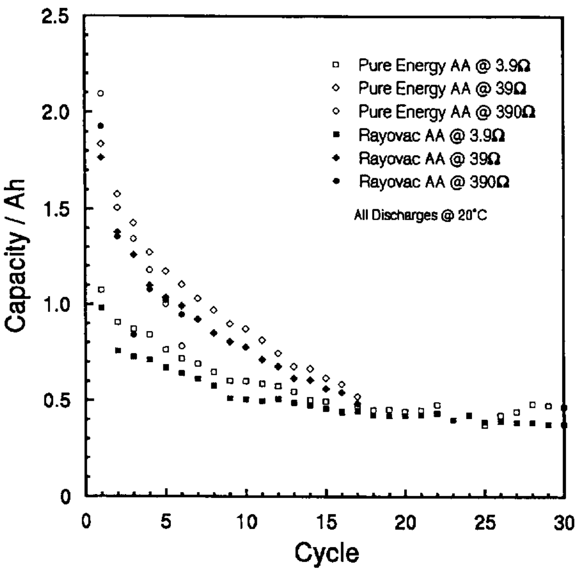

Fig. 3. Ah capacity at 20°C of Pure Energy and Rayovac AA cells at three different rates of discharge. All cells charged at room temperature for 12 h using their respective commercial pulse chargers.

To date only 15 cycles of medium rate discharges are complete and only 5 cycles of low rate discharges of the AA cells. Nominal rates were completed to 30 cycles.

Fig. 3 illustrates that cell capacity per cycle approached the theoretical 'first electron' capacity in the medium and low rate experiments. When compared to the 3.9 ohm capacities for the experiments completed so far initial cycle capacities almost doubled on low rate and medium rate discharges.

During the 6th cycle on 390 ohm loads, all three Pure Energy AA cells failed. It has been suggested that this is a consequence of the no-mercury formulation [5]. Experiments on D cells are in progress. Cells on 22 ohm loads have completed 10 cycles and cells on 220 ohm loads have completed 2 cycles.

3.6. Failure mechanisms

Failures of RAM products were few during the cell testing. The predominant mode of failure was leaking. The Rayovac D product was most susceptible to failure in these studies. The Pure Energy AA rarely failed (four cell failures). Three cells failed on 390 ohm discharge at 20°C upon completion of the 6th cycle. One cell failed during 50°C storage for 60 days. Leaks formed between the brass current collector and the end cap. Pure Energy has recently instituted a change in the production of this sub-assembly [6]. The Rayovac AA cells have not failed to date.

3.7. Other RAM cell observations

The capacity of an RAM cell decreases on every cycle. In multi-cell applications, it is important to keep the cells all at a balanced capacity throughout their useful service life. Ensuring that all of the cells are treated the same electrically is the obvious solution. Using commercial chargers, where cells are charged individually, opportunity for mismatching cells arises. 'Bundling' (connecting) cells together to form a multi-cell battery is therefore recommended. This creates a need for a battery charging system. Multi-cell batteries are the focus of the remaining studies.

Based upon the early results of some of the multi-cell experiments, it appears that shallow discharges increase the cycle life of RAM cells. A good policy to follow when using RAM cells is to charge them at every opportunity. This is opposite to accepted good practice with nickel/cadmium where it is advisable to deep discharge from time to time. This is an important educational issue when introducing RAM technology to users for the first time.

RAM cells are advertised as being capable of delivering more than 25 cycles. How many more? Fig. 4 shows that cells can be cycled well past 25 cycles. These cells were charged at room temperature (LED limited) in their commercial

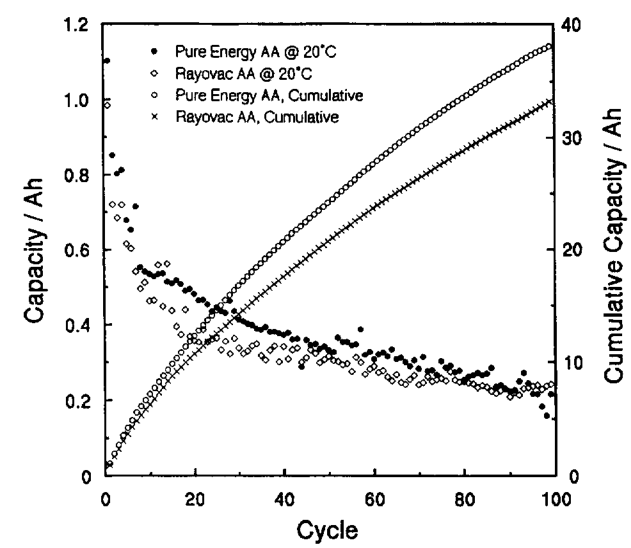

Fig. 4. Pure Energy and Rayovac AA cells: continuous 3.9 ohm load, 20°C. Charger-limited charge at room temperature with commercial pulse chargers.

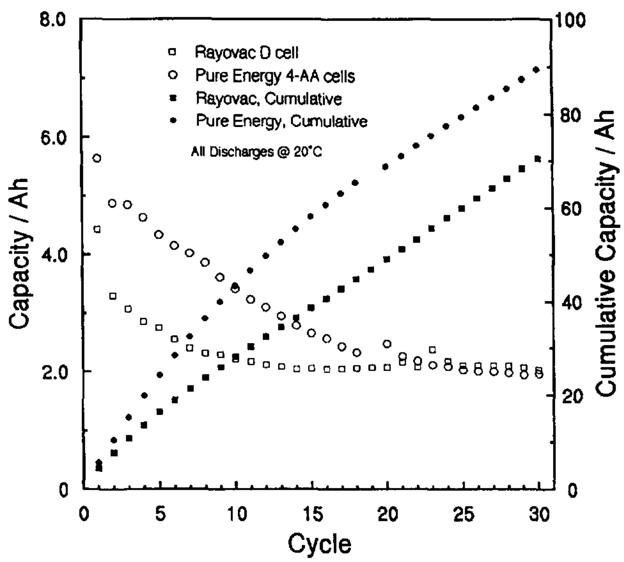

Fig. 5. Comparison of four Pure Energy AA cells in parallel vs. a single Rayovac D cell (result is the average of three cells): continuous 2.2 ohm load, 20°C, automated cycler (d.c. taper charge limited to 1.65 V, 400 mA).

chargers and discharged at 20°C. The rate of diminishing capacity drops off and the cells seem to be capable of many low-capacity cycles. This was a surprising result, as one manufacturer had suggested that the product would likely fail shortly after 25 full cycles due to separator breakdown. Research into raising the delivered capacity after 30 cycles from the current level of 300–400 to 600 mAh or more is in progress [5].

Kordesch had suggested that four AA cells in parallel are superior in performance to a single D product. The MnO_2 pellets in the D cell are thicker and ionic diffusion is less efficient as a result. Building battery packs out of AA cells rather than C or D cells has been suggested. A simple experiment was conducted to compare four AA cells in parallel and to a single D cell by substituting four AA cells for a D cell with all other conditions kept the same as for the standard D cell experiment (2.2 ohm, 1.65 V, 400 mA limits, 20°C). The results are presented in Fig. 5. If the current had been higher, the comparison would have been even more dramatic according to Kordesch.

4. Summary

As this is a report on work in progress, it is premature to attempt to definitively answer the question of RAM technologies future role in the C.F. The results presented herein speak for themselves. In general, the performance of RAM technologies today appears to be in accord with manufacturers claims for the technology. In our experience, this is not always the case with new battery technologies so few years after commercial release [7]. The use of RAM in the C.F. may rest upon the success of RAM battery packs more than cell performance. Studies in progress will hopefully shed light on the potential of RAM battery packs. There are user education issues to be addressed in order for the full potential of RAM technology to be realised, not unlike any other battery technology.

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