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Rechargeable alkaline manganese dioxide/zinc batteries

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Abstract

The rechargeable alkaline manganese dioxide/zinc MnO_2/Zn) system, long established commercially as a primary battery, has reached a high level of performance as a secondary battery system. The operating principles are presented and the technological achievements are surveyed by referencing the recent publications and patent literature. A review is also given of the improvements obtained with newly formulated cathodes and anodes and specially designed batteries. Supported by modelling of the cathode and anode processes and by statistical evidence during cycling of parallel/series-connected modules, the envisioned performance of the next generation of these batteries is described. The possibility of extending the practical use of the improved rechargeable MnO_2/Zn system beyond the field of small electronics into the area of power tools, and even to kW-sized power sources, is demonstrated. Finally, the commercial development in comparison with other rechargeable battery systems is examined.

Introduction

Manganese dioxide/zinc batteries (MnO_2/Zn) are well known to be product leader in the primary battery market. Once the older Leclanché cell (inside cathode, 'bobbin-type') could be improved to the high-drain alkaline MnO_2/Zn cell (sleeve-type, outside cathode) [1–3], this battery system conquered the market due to some excellent qualities such as inexpensiveness, good shelf life; high-temperature performance and, with increasing public awareness, its environmental friendliness.

To change a primary battery system with such outstanding positive features into a secondary battery type was a technical challenge. In 1977, following early development work at Union Carbide Corporation, research was intensified at the Technical University of Graz (TU Graz), Austria, and new cell designs started to appear in the early 1980s [4]. Further development of the rechargeable MnO_2/Zn system was performed in specific projects that were funded by the Austrian Funds for the Support of Scientific Research.

Over the last few years, advancement of the technology of the rechargeable alkaline manganese dioxide (RAM)/zinc battery has progressed rapidly. Intensive research activities at the TU Graz and development efforts at Battery Technologies Inc. [5] have resulted in considerable improvements [6]. Between 1989 and 1992, the cycle capacity has been more than doubled, and the mercury addition to the anode has been gradually reduced and finally eliminated (Fig. 1). Today, the excellent elevated temperature shelf life, which is expected from alkaline MnO_2/Zn primary cells, is also a feature of RAM batteries [7].

The technology has been licensed to Rayovac, USA. After extensive testing and market surveys in 1992–1993 (Fig. 1), the mass production of RAM batteries started

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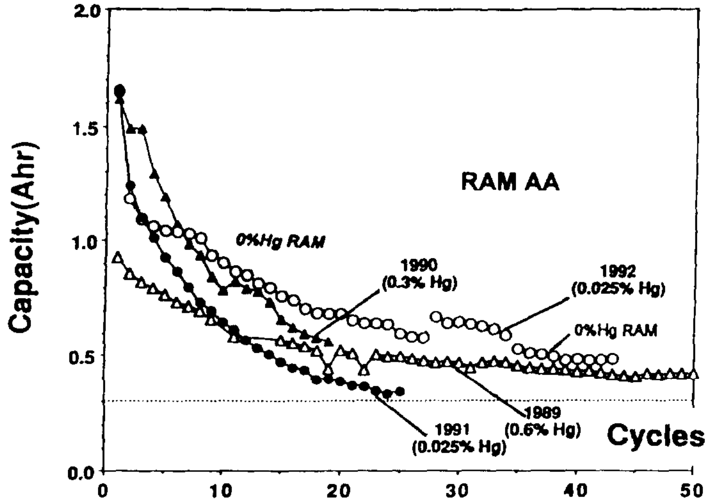

Fig. 1. Progress of RAM batteries during 1989 to 1992.

TABLE 1

Characteristics of MnO_2/Zn system

Cathode	manganese dioxide (MnO_2)
Anode	zinc (Zn)
Electrolyte	potassium hydroxide (KOH)
Open-circuit voltage (OCV)	1.55 V
Theoretical energy density	290 Wh kg^{-1}
Practical energy density	77 Wh kg^{-1} or 215 Wh dm^{-3}

in autumn 1993. Under the trade name 'RENEWAL', four types of cylindrical cells were made available to the consumer market as 're-usable' batteries, together with special charging stations.

Operating principles

The important parameters of the alkaline MnO_2/Zn system are listed in Table 1.

A cut through an AA-sized RAM cell is shown in Fig. 2. The cathode consists of four pressed pellets. These consist mainly of manganese dioxide, but must at least contain graphite because of the low conductivity of the former material. The zinc anode is usually built as a gel electrode.

The discharge reactions in chargeable alkaline MnO_2/Zn cells are principally the same as in the primary cell. The cell reactions can be simplified as:

(i) cathode $2MnO_2 + H_2O + 2e^- \longrightarrow Mn_2O_3 + 2OH^-$ (1)

(ii) anode $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$ (2)

(iii) total $Zn + 2MnO_2 \longrightarrow ZnO + Mn_2O_3$ (3)

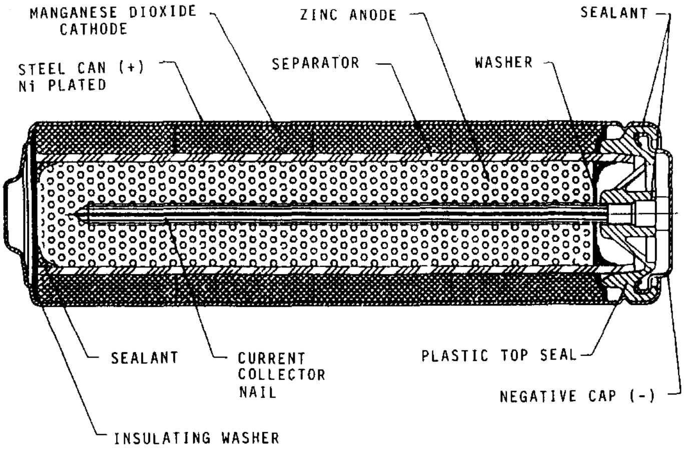

Fig. 2. Cut-through section of an AA-size rechargeable alkaline MnO_2/Zn cell.

The most important difference from the discharge of a primary cell is that in the rechargeable cell only the first electron of the manganese dioxide is allowed to be discharged. The discharge of the second electron leads to soluble Mn(II) species. The first electron discharge proceeds via the homogeneous proton-insertion path and four-valent manganese dioxide is formally reduced to $MnO_{1.5}$, i.e.:

$$MnO_2 + H_2O + e^- \longrightarrow MnOOH + OH^- \quad (4)$$

To ensure that the second electron is not discharged, a 'chemical switch' is provided by using a zinc-limited anode. The first-cycle capacity of a RAM cell is close to the capacity of primary cells, because the second-electron capacity is not used in most applications due to the low voltage versus zinc.

An important point for the satisfactory operation of the cell is the availability of sufficient amounts of hydroxide ions (KOH), especially in the anode. Zincate is formed during the initial discharge process, i.e.:

$$Zn + 4OH^- \longrightarrow [Zn(OH)_4]^{2-} + 2e^- \quad (5)$$

Zinc oxide is produced either by deposition from the zincate, setting OH^- ions free (a very beneficial reaction) or by direct oxide formation:

$$[Zn(OH)_4]^{2-} \longrightarrow ZnO + 2OH^- + H_2O \quad (6)$$

$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^- \quad (7)$$

The main processes in the porous gel anode are illustrated in Fig. 3.

During the charging of the cell, the upper reactions are reversed. Constant-voltage (tapering current) charging (1.65 to 1.72 V) is generally recommended for RAM cells. Such chargers are essentially low-cost devices. For fast battery charging, more expensive pulse-current chargers with resistance-free voltage sensing have been used successfully [8, 9].

To prevent zinc dendrites during the charging, RAM cells have a separator made of cellulose and an additional layer made of fibre material. It is possible to combine these two layers in a laminated separator that cannot be pierced.

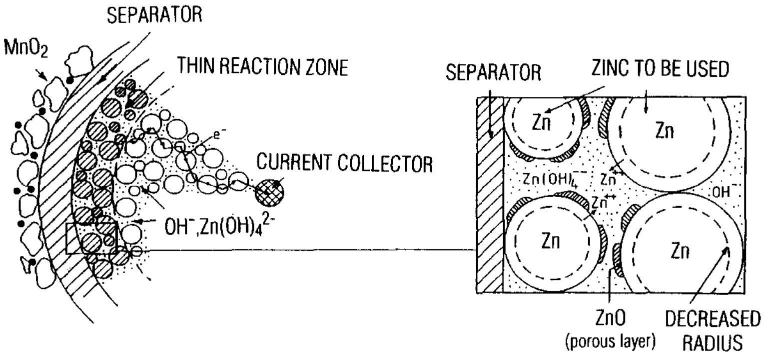

Fig. 3. Illustration of main processes in a porous zinc gel anode.

Current status

The cumulative performance of AA-sized RAM cells is presented in Figs. 4 and 5. Depending on the mode of operation, more than 1700 service hours (intermittent service) can be obtained. As an estimate, one rechargeable AA-cell can replace 20 primary alkaline cells and 80 zinc/carbon cells in the deep-discharge mode (cutoff voltage of 0.9 or 0.8 V).

The advantages and disadvantages of the RAM MnO_2/Zn system are listed in Table 2. (Note, the expression 'rechargeable primary cell' is sometimes used. This is generally incorrect and should be discouraged.)

The discharge curves of AA-sized RAM cells on continuous discharge at various loads at 20 °C are given in Fig. 6. After about 20 cycles, the capacity asymptotically reaches a 'rest' capacity of roughly 0.5 Ah. This long-cycle plateau can reach up to 100 (or more) cycles. Counting accumulated capacity figures, more than 30 primary alkaline cells can be replaced by one RAM cell. (Note, commercial AA-nickel/cadmium cells are rated between 0.5 and 0.8 Ah, fully charged.)

Figure 7 gives the logarithmic increase in service hours with decrease in the depth-of-discharge (compare also walkman service hours in Fig. 5). After 500 cycles, a 'plateau capacity' of 0.3 to 0.5 Ah remains; the value depends on the design and additives. It appears that their capacity is not lead sensitive; it may consist of heterogeneous MnO_2-phases that contain zinc in the form of hetaerolite.

The first main disadvantage, the adverse effect of the depth-of-discharge on the cycle life, can be influenced by changing the battery design. For the present design, it is obviously best to recharge the cell as many times as possible, even when it is not 'exhausted'. For OEM (original equipment manufacturing) applications, however, it will probably be the better to use less zinc in the cell so that the cathode (which causes this problem) can never be discharged too deeply.

Several attempts have been made to overcome the second main problem, which is the fading of capacity on higher loads. To make the RAM system usable for high-power applications a 'non-chemical' solution has been found. In at least half of the high-power applications, which presently employ C- or D-size nickel/cadmium batteries, it is possible to use 'RAM-bundle cells' of the D- or C-size, which are simply 4 AA and 4 AAA cells in parallel arrays, fitted into an outer container of the same dimensions. With this arrangement, the current is 'divided' and each cell in the container has to carry only a quarter of the load. Moreover, another reason why bundles of small

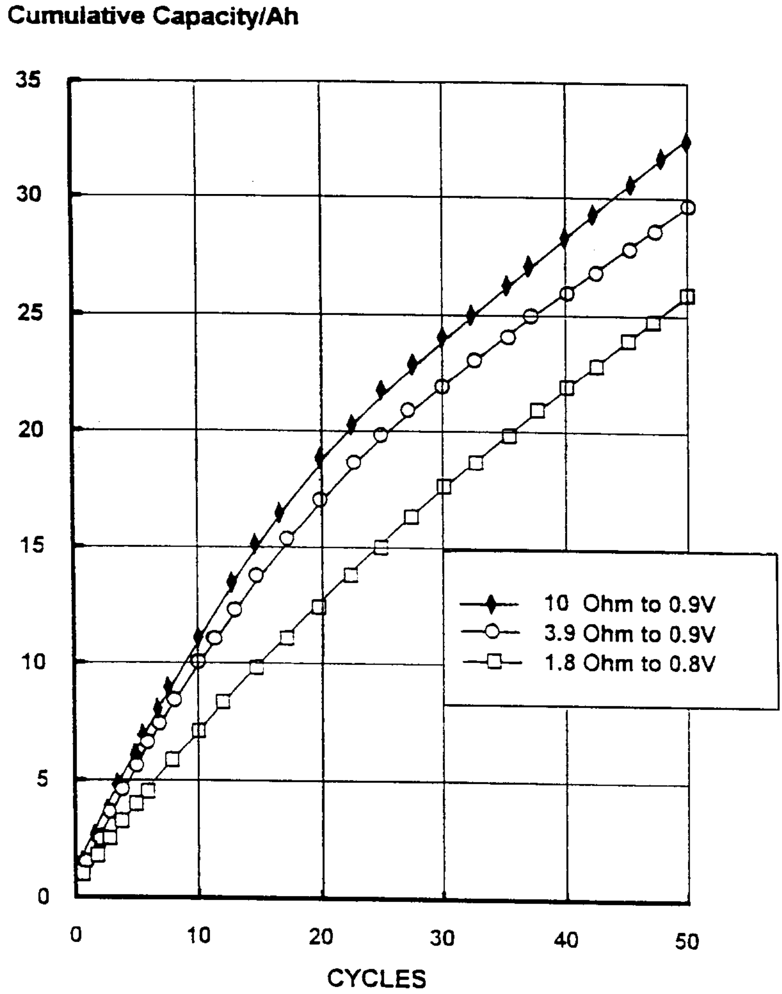

Fig. 4. Accumulated capacity of RAM AA-cells on deep discharge.

cylindrical cells work much better than the larger diameter cells in heavy-duty applications is that the multiple thin-layer cathodes and the larger interface between MnO_2 and the powdered zinc anode allow a much higher utilization of the MnO_2 and also of the zinc gel structure. The advantages of connecting AA cells in parallel to replace the larger D cells are demonstrated in Fig. 8. It should be pointed out, however, that these cells will not be able to compete in the extreme high-power output range with the spirally-rolled electrode constructions of the present nickel/cadmium or nickel/metal hydride cells, but they could claim at least 50% of the high-performance market for these systems.

In order to satisfy the market for medium-sized electric power supplies for applications in the 100 W to 1 kW range (where presently lead/acid batteries are used), higher voltage units (6, 12 and 24 V) are required. In such batteries, the required number of cylindrical AA cells are arranged in parallel 'bundles', then spot-

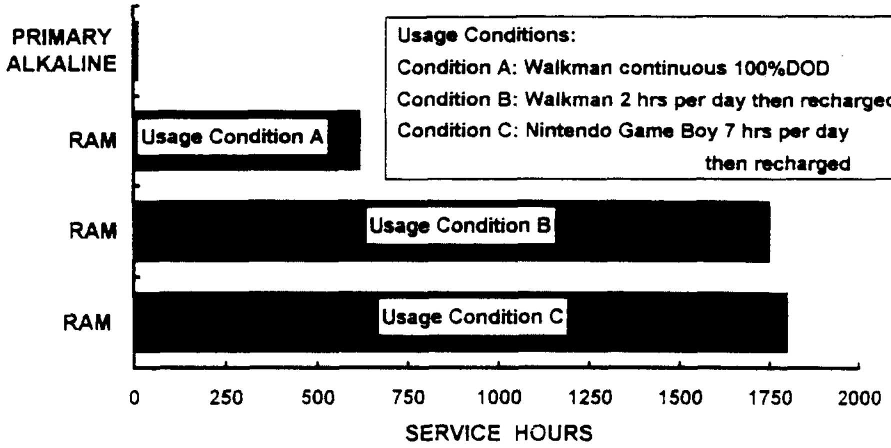

Fig. 5. Total service time of rechargeable alkaline manganese dioxide/zinc cells (AA-size) compared with primary alkaline cells and for various usage conditions.

TABLE 2

Major advantages and disadvantages of state-of-the-art rechargeable alkaline MnO_2/Zn batteries

Advantages	Disadvantages
Environmentally friendly Low manufacturing cost Directly interchangeable with primary cells Completely sealed, maintenance free Excellent shelf life Good temperature performance	Cycle life and Ah capacity decrease with depth-of-discharge and load

welded to top and bottom metal sheets (or strips) by a fully automatic procedure. The parallel modules are then arranged in series for any voltage required. Figure 9 shows the design of 6 or 12 V, 0.5 kW batteries by using series-connected 'bundle cells' of nominal capacity: 50 Wh kg^{-1} [10].

Technical challenges

The above-mentioned problems are the subject of intensive investigation. The origin of these disadvantages has to be determined and remedies have to be found without affecting the main qualities of the RAM system, namely, low cost and environmental friendliness.

One main emphasis of the research is the cathode. It has been shown [11, 12] in experiments with cells containing a surplus of zinc that characteristics such as the capacity dependence on the depth-of-discharge and the load are typical manganese dioxide electrode features.

A cathode discharge model, developed at the TU Graz [13], points to the different electronic and ionic pathways in thick cathodes that consist of a MnO_2–graphite mix. The manganese dioxide is a poor conductor and depends on the graphite to transport

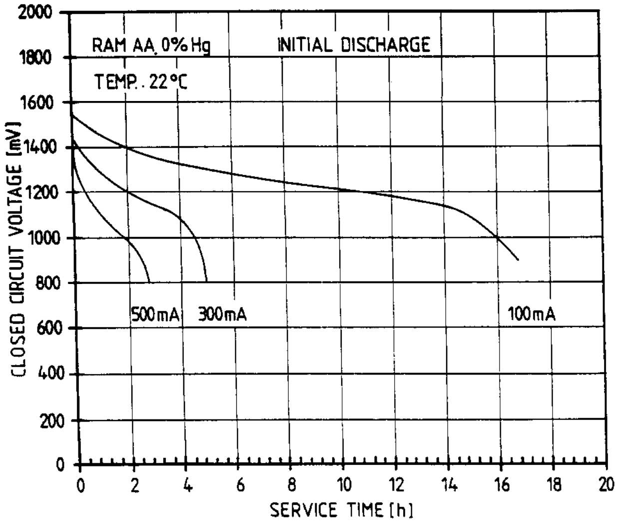

Fig. 6. Typical discharge curves for mercury-free rechargeable manganese dioxide/zinc (RAM) cells. Cell size: AA (LR6); constant current from 100 to 500 mA. Curves show first discharge cycle.

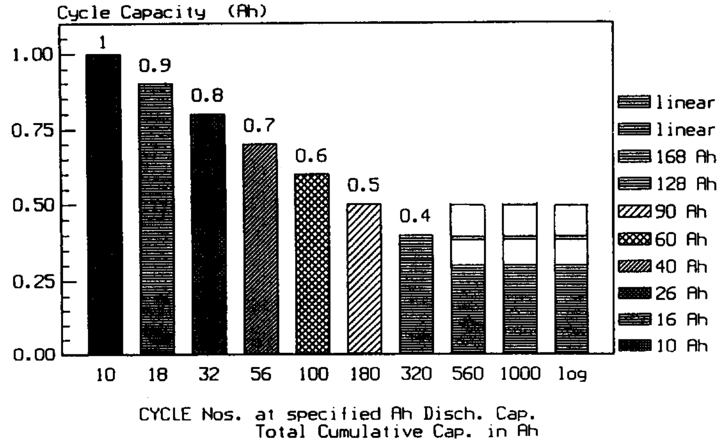

Fig. 7. Schematic diagram that describes the logarithmic increase in cycle number with decreasing depth-of-discharge. After 500 cycles, a 'plateau capacity' of 0.3 to 0.5 Ah remains, depending on design and additives. This capacity seems not to be load-sensitive; it may consist of heterogeneous MnO_2 phases that contain zinc in the form of hetaerolite.

the electrons to the interface, while the KOH that fills the pores system provides the ionic supply. Ideally, the two pathways should be as close as possible in their conductance values (Fig. 10). To increase the conductivity of the cathode has been a research objective for a long time. According to this model, the conductivity cannot be increased by using more or better conductive additives only. It is necessary to improve the ionic conductivity at the same time. Now, it seems obvious why the greatest improvement in capacity and short-circuit current of RAM cells was reached by using a filler

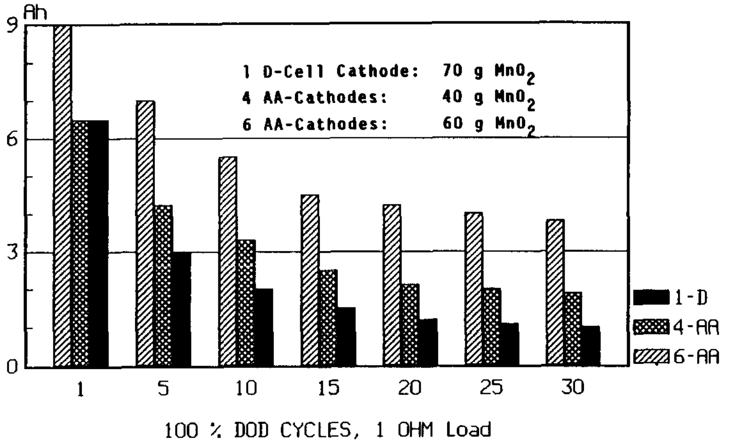

Fig. 8. Advantages of parallel-connected AA cells over D cells. 'Power cell': 4 AA cells fit exactly into 1 D-cell container.

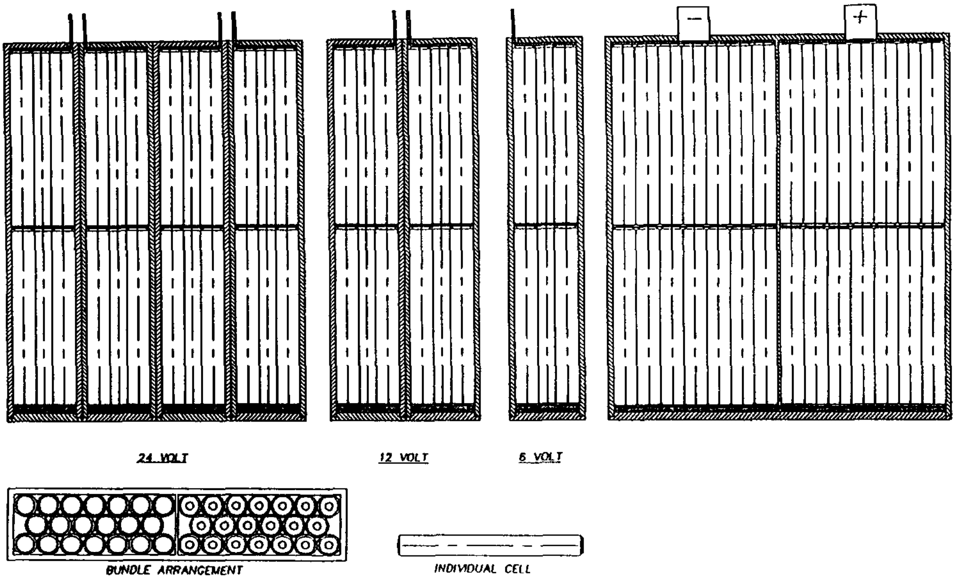

Fig. 9. Design of larger batteries by connecting 'bundle batteries' in series. Nominal capacity: 50 Wh kg^{-1}.

substance (Fig. 11) [14]. The ionic conductivity was increased by providing 'space' for the KOH supply.

For further progress, both the electronic and the ionic conductivity have to be improved simultaneously. Should the electronic conductivity be improved alone, the result would be an even higher efficiency of MnO_2 reduction near the separator and a lower utilization at the steel can collector side. Actually, the MnO_2 at the separator side is sometimes reduced below the one-electron level; this causes irreversible oxides to be formed. Thus, it will be very important to find a way to produce cathodes of

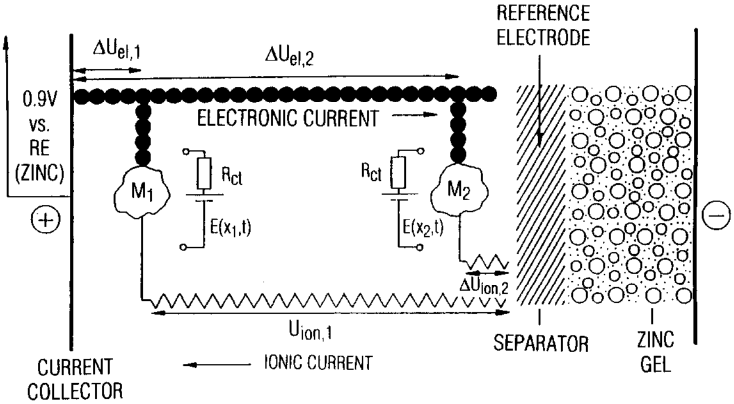

Fig. 10. Illustration of differences in the local electrochemical potential in porous cathode of an alkaline manganese dioxide/zinc cell. Most uniform discharge occurs when values of ionic and electronic conductivity are similar throughout the cathode.

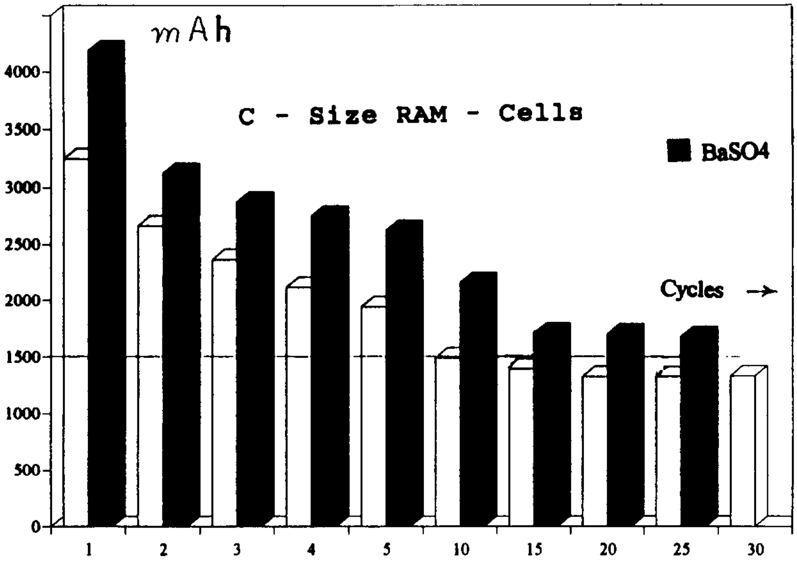

Fig. 11. Effect of adding a porous filter to the cathode mass.

a high porosity. (Note, in a volume-limited cell, the electronic conductivity cannot be increased by simply adding more graphite to the cathode, because the energy density would drop due to the low specific weight (density) of graphite (less space for active material.)

An ageing problem that causes both loss of capacity and increase in cell internal resistance is poor wetting of the graphite by the electrolyte. Thereby, the contact between MnO_2 and graphite is probably lost. Addition of a small percentage of a wet-proofing agent is helpful in this case.

The model also explains why the utilization of the MnO_2 is better in cell dimensions with thinner cathodes. The 2 mm thin cathodes of the AA cells are far more uniform with respect to electronic and ionic conductivity and, for this reason, are more efficiently discharged than the C- and D-cathodes (4 and 6 mm thick). If it is possible to build more porous and still high conductive cathodes the layers in all cell dimensions can be made thicker, which means that the cell has a higher Ah capacity.

A second problem can be solved in the following way. As a RAM cell is zinc-limited, but the cathode thickness should be kept small, there is too much space for the anode. It is generally believed that there can never be sufficient space for a 'KOH reservoir', but in fact the zinc density in the gel is of dominant importance. Besides the hydrogen corrosion, many problems were covered up in mercury-containing zinc gels. Now that it is not permissable to add mercury, the qualities of mercury with regard to connecting the zinc particles by building up 'bridges' have become noticeable. In an electrode with a low zinc density, this problem is of course more severe than in a primary-cell zinc anode. The loss of the particle-to-particle connection is revealed dramatically in drop tests, but leads to a lower short-circuit current. If it could be managed to build thicker cathodes with satisfactory qualities, there would be less space for the anode. The latter would have to be more dense (i.e., higher zinc contents).

Further anode research is directed towards the development of a conductive net throughout the anode. In the present gel anode, the zinc serves as both an active material and a conductive screen. This works because there is always, even when the cell is discharged, some zinc remaining in the gel due to incomplete usage. From this point of view, the limited zinc utilization due to zinc passivation under increasing loading is a positive effect. But of course it would be much better to have a stable conductive net that connects the zinc particles, (ideally) independent of different current densities. The addition of copper powder or silver-plated plastic fibres serves this purpose very well [15, 16], but this would require addition of mercury. Because zinc is thermodynamically unstable in aqueous solutions, it is not easy to find suitable conductive additives that would not lower the kinetic inhibition of hydrogen evolution. It was shown [13, 17] that the addition of graphite improves considerably the qualities of zinc electrodes with respect to capacity and cycle life, but it was not possible to suppress the higher gassing rate in such cells. For this reason, the use of graphite in the anode has not yet proved successful for hermetically sealed cells. Nevertheless, this is still a promising field, especially because zinc electrodes are used in several other alkaline battery systems.

Typically, RAM cells exhibit a large decrease of capacity in the initial 10 to 20 cycles followed by a constant plateau. The charging factor (quotient of charging capacity and discharge capacity) is below 1 until the plateau is reached. It is not possible with the present charging methods to return the same amount of capacity to the cell that was taken out previously. Higher charging voltages have been examined, but charging manganese dioxide to higher voltages produces 6-valent manganate, which is soluble and disproportionates into MnO_2 (of the rechargeable type) and a non-rechargeable lower oxide. Therefore, it is more important to prevent the formation of manganate by limiting the charge voltage to about 1.65 to 1.72 V. It was also found, however, that certain catalysts prevent manganate formation and cause a nearly stoichiometric evolution of oxygen [18, 19]. Figure 12 indicates the initial delay of oxygen evolution on overcharge and the effect of catalysts. It can be concluded that charging to about 1.9 V produces Mn(VII) species that disproportionate to MnO_2 and oxygen [20].

For the use of such catalysts in a sealed cell, a way must be found to accept the evolving oxygen within the cell. An easy way would be the reaction of oxygen and zinc where ZnO is formed. Therefore, a good access to the zinc surface must be guaranteed as, for example, in a highly porous electrode. A way to facilitate the uptake

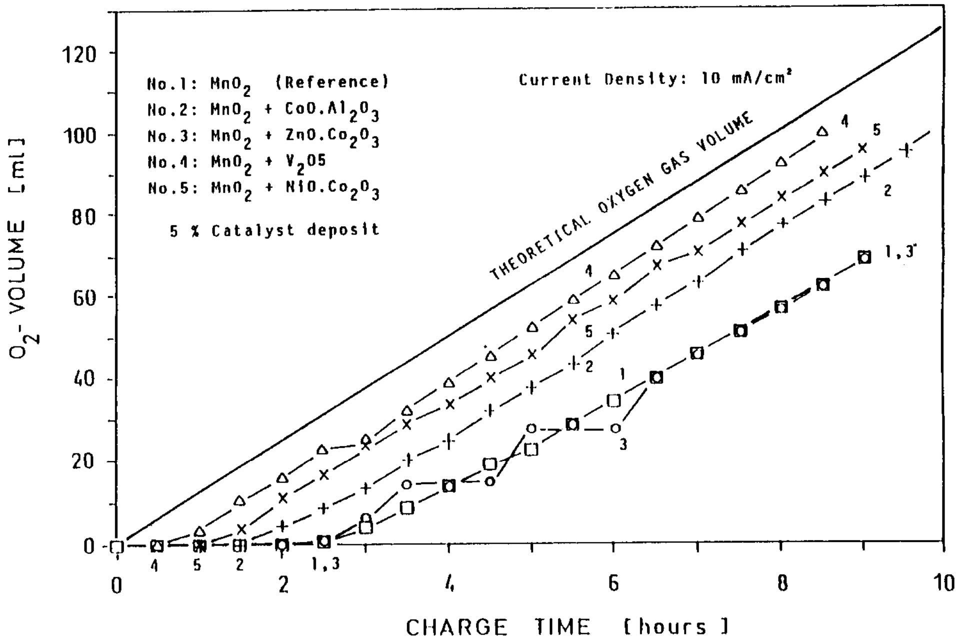

Fig. 12. Changing oxygen-evolution efficiency by adding catalysts.

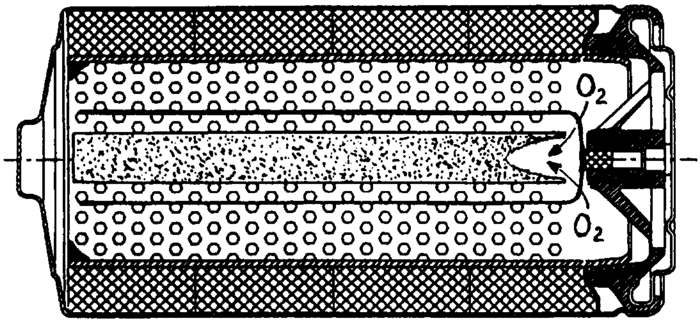

Fig. 13. Design of a C-sized RAM cell with a porous cylinder in the centre of the anode to facilitate oxygen-gas reaction with zinc.

of the oxygen gas is to insert a porous cylinder in the centre of a gel anode (Fig. 13) [21]. The system is self-regulating, as the gas reaction is favoured with increasing pressure. If a cell can be built with a safe oxygen-circulation mechanism, it might be possible to increase the charging factor in the earlier cycles and, therefore, prevent capacity loss.

Furthermore, the charging time would be shorter due to the higher charging voltage or current. For batteries of several cells (bundles cells), it is of special importance that the cells are equal in capacity. The oxygen-accepting cell would not only decrease the probability of leakage, when a cell is reversed, but provide a more equal starting position after every charge.

Commercial impact

The worldwide battery market is estimated to provide revenues in the order of US$ 26 billion annually. It can be divided into roughly equal two parts, a 'large format market', and a 'small format market'. The first includes automotive lead/acid and other industrial-type rechargeables. These estimates exclude the former USSR, China and the Eastern Block countries, which will probably experience an avalanche of market development in the years ahead. The rapidly increasing consumer electronics market is responsible mainly for the large expansion in the 'household use' of batteries. The market requires batteries for toys and games (21%), flashlights (16%), cameras (12%), radios (12%), cassette recorders (12%), calculators, shavers and others. The division and growth potential of the two segments of the worldwide market, are shown in detail in Table 3. Figure 14 illustrates the worldwide 'household battery market' and the types of primary and secondary batteries that are used.

Alkaline MnO_2/Zn batteries and heavy-duty zinc/carbon (Leclanché) batteries are the dominant types in the 'household market'. Together, these two systems account for about 90% of the market. Duracell, Eveready and Rayovac are the main producers in the USA, and 80% of the batteries are sold through retail discount, food and drug stores. The majority is sold to the 'heavy household user group' which consumes 96 batteries per year. It is represented by a family with two children (6 to 12 years old) or two young adults (13 to 20 years old). The rest is sold to the 'average household', which consumes 36 batteries per year. The market shares of manufacturers (in units) of alkaline and heavy-duty zinc/carbon batteries are shown in Table 4.

During 1992, a considerable growth rate in the market share was experienced by Rayovac, a privately owned company. Rayovac licensed the RAM technology and after extensive testing and market surveys in 1992–1993, the mass production of RAM batteries started in autumn 1993. Under the trade name 'RENEWAL', all four types of cylindrical cells were made available to the consumer market as 're-usable' batteries, together with special charging stations. Rayovac is least effected by the replacement

TABLE 3

Worldwide battery market

Market type and size	$ (Billion)	Growth % per year
Small format market		
Consumer electronic	10.0	6%[a]
High performance	3.0	25%
Large format market[b]		
Automotive lead/acid	7.0	small + %
Other rechargeables	4.0	high + %
Military/space	2.0	lower − %

[a] Adding the (not included) Third-World markets, the low-segment of the consumer electronic market is expected to grow perhaps twice as fast with a lesser demand for expensive high-power batteries. A growth of 10 to 12% per year is a reasonable prediction.

[b] The electric vehicle propulsion battery market is not included. It may involve a doubling of the lead/acid battery production facilities and corresponding investments within a few years. If 'other' systems, such as nickel/cadmium and nickel/metal hydride are chosen, their market will grow strongly, but will be restricted by the high cost of these systems. The zinc/bromine system recently improved its chances against high-temperature systems such as sodium/sulfur.

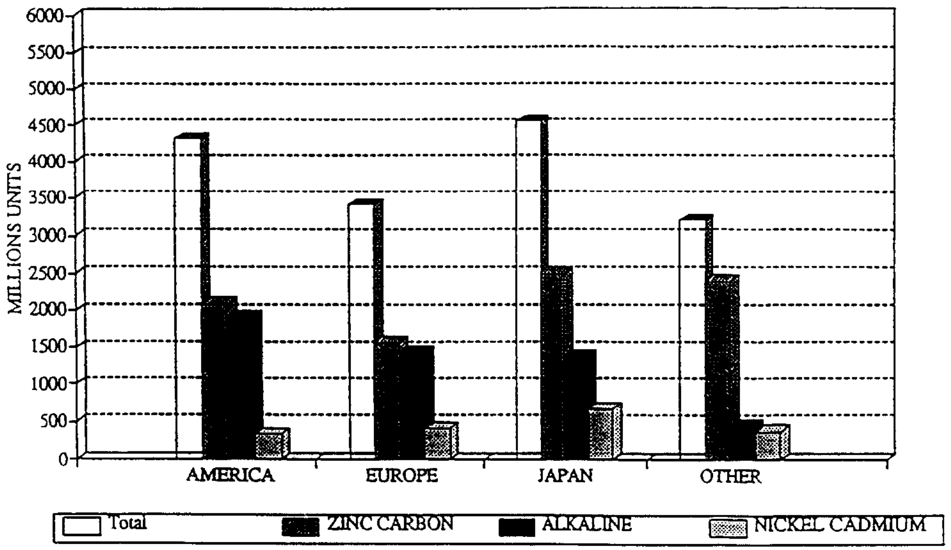

Fig. 14. 1990 worldwide 'household battery market' and number of units of primary and nickel/cadmium batteries used.

TABLE 4

Consumer electronics market share data[a]

Producer	Alkaline (%)	Heavy duty (%)	Total (%)	Sales ($\times 10^9$ US$)
Duracell	45.2	2.3	37.6	1.6
Eveready	34.4	41.7	35.7	1.8
Rayovac	12.6	49.7	19.2	0.6

[a]Source: A.C. Neilson Rating, 1992.

of disposable alkaline primary cells with low-cost re-usable and completely interchangeable alkaline cells, because their percentage of the alkaline primary cell market is comparatively low.

About 13 billion primary MnO_2/Zn batteries are manufactured and thrown away per year. It should be obvious that 'environmentally friendly' products are a good business nowadays, where the 'environmental awareness' of people is constantly growing and even developing into a strong political movement. The RAM cell is a rare example of a product that can save resources and avoid waste without causing higher expenses for the consumer. The fabrication of RAM cells can be done on essentially the same machinery as is used for the production of primary cells (at nearly the same costs), which should make a start really attractive for experienced manufacturers of primary cells. A fully operational plant produces over 200 million batteries per annum. Figure 15 shows part of an automatic assembly line as it is offered by HIBAR Systems Ltd., Richmond Hill, Ont., Canada.

Concerns about expensive chargers can be put aside. Chargers with constant-voltage circuits, as generally recommended for RAM cells, are essentially low-cost

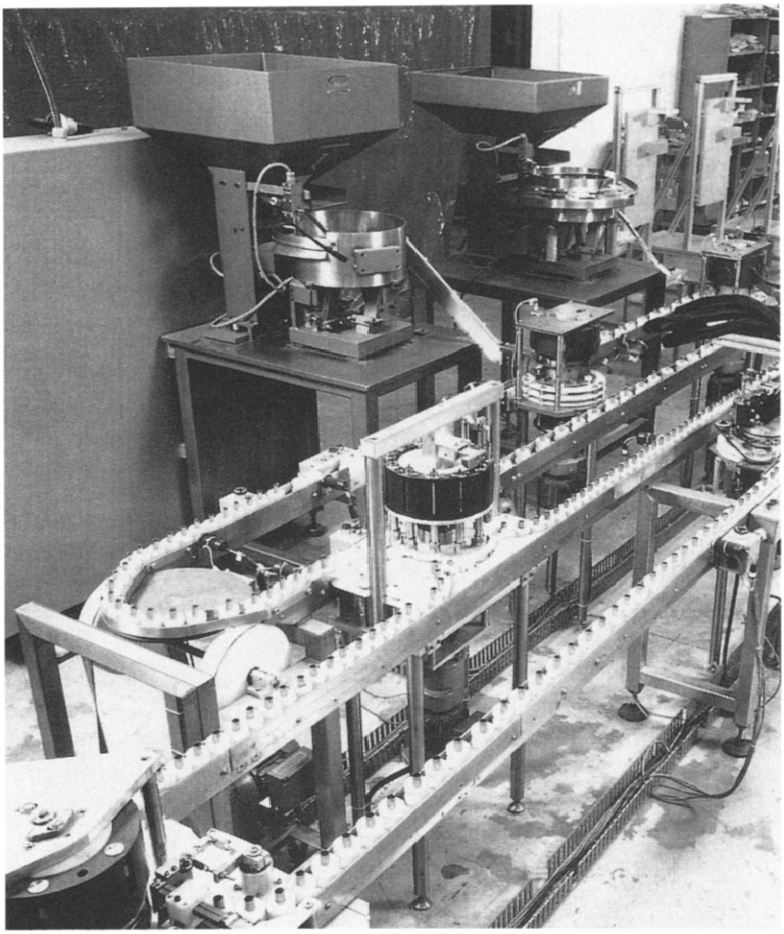

Fig. 15. Part of an automatic assembly-line as built by HIBAR Systems Ltd., Richmond Hill, Ont., Canada.

devices. The smaller Rayovac charger, which is good for four AA- or C-sized cells, costs US$ 15. This charging station controls each cell separately and has a mechanical safety precaution that prevents the charging of a primary cell. The low-current charging of two cells in series, as it is common practice with many small chargers of the nickel/cadmium type, can be applied if a current overflow-path is provided, e.g., by a suitable zener diode. In this way, a charger could be designed that would be universally usable for nickel/cadmium, nickel/metal hydride and MnO_2/Zn batteries (Fig. 16). Photovoltaic chargers are also feasible. A typical application of the overflow electronics is shown in Fig. 17. Two AA nickel/cadmium cells were replaced by two AA-sized RAM cells in a hand torch with an integrated charger.

RAM cells will not only extend the secondary battery market by replacing primary MnO_2/Zn batteries, but will outperform other rechargeables, such as nickel/cadmium and nickel/metal hydride cells, in many applications. The most noticeable and consumer-relevant advantage over other types of rechargeable batteries is the good shelf life at

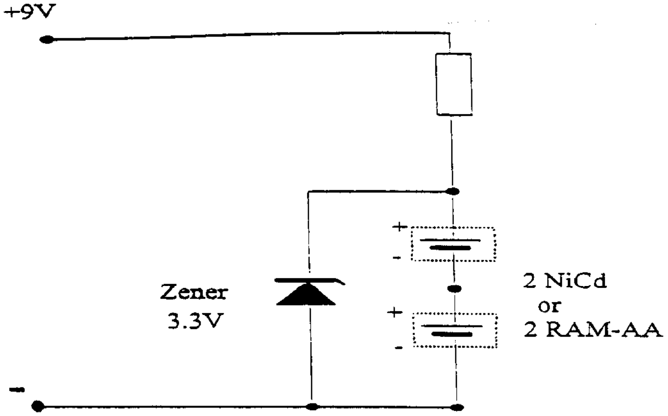

Fig. 16. Principal overflow protection with a 3.3 V zener diode applied to two RAM or two nickel/cadmium cells in series.

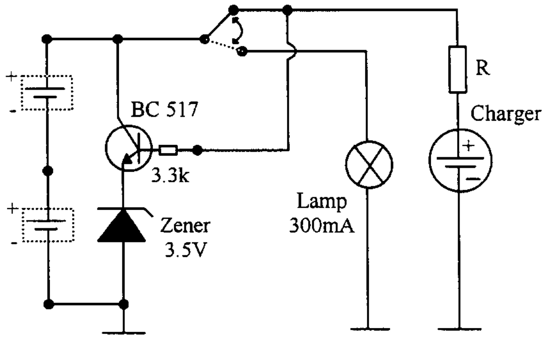

Fig. 17. Stand-by lamp changing circuit with two AA-sized RAM cells as replacement for two nickel/cadmium cells in a radio schack hand torch.

elevated temperatures. Particularly in summer at high temperatures, other rechargeables are only of restricted use due to their high self-discharge rate. Figure 18 presents a comparison of test results achieved at 65 °C with RAM cells, nickel/cadmium and nickel/metal hydride cells. These (Arrhenius law) data, expressed in weeks of storage time, can also be used to predict the room-temperature shelf life for the respective numbers of years. This is a well-established rule in the battery industry. Figure 19 illustrates the rapid self-discharge of nickel/metal hydride cells at elevated temperatures [22].

The typical field of applications of RAM cells covers not only the consumer market for toys and games, flashlights, cameras, radios, tape recorders, calculators, lamps, shavers, small computers and other similar gadgets, but also 'high-power applications' such as hand tools (e.g., drills), high-powered hand lanterns, portable electric typewriters and, possibly, heavy-duty telephone communications equipment and portable computers. Camcorders are presently on the edge of the user range for cylindrical RAM batteries; they need continuous deep-discharge capabilities, and rolled and bipolar cell designs are better suited [23, 24]. Furthermore, emergency lighting,

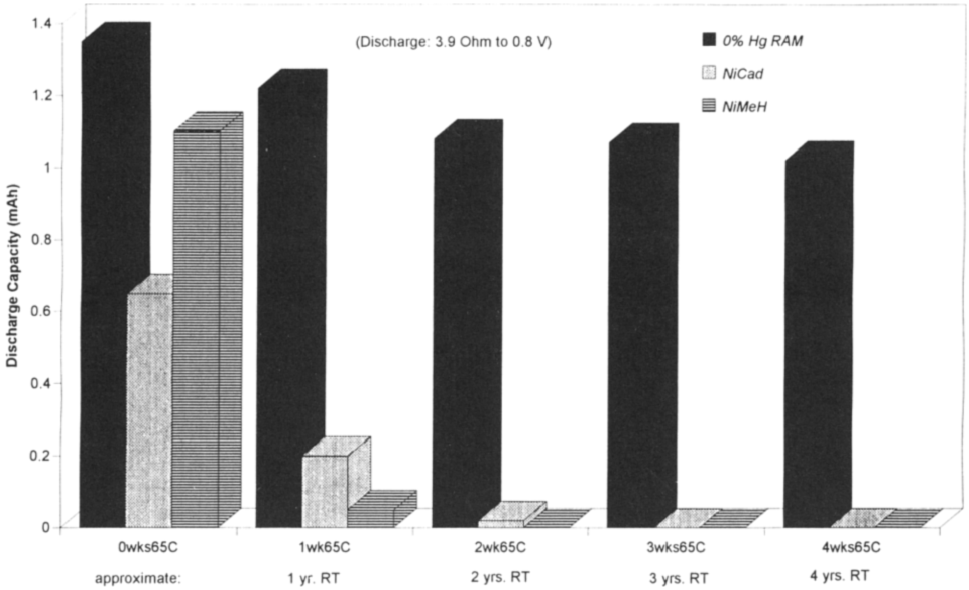

Fig. 18. Comparison of initial capacity and performance losses of different rechargeable battery types at 65 °C.

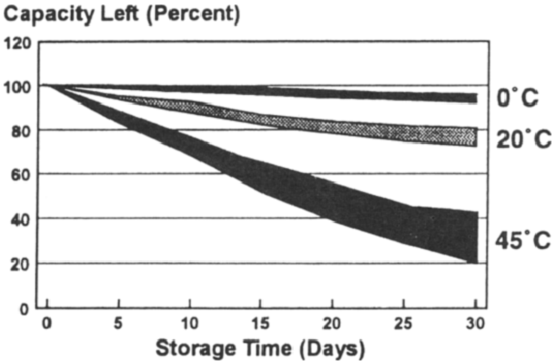

Fig. 19. Illustration of rapid self-discharge of nickel/metal hydride cells at elevated temperatures [22].

solar power stations, shopping carts, wheelchairs, electro-scooters and even lawn-mowers have been tested within the bundle-cell project.

The still wide-open field of electric-vehicle batteries is filled with predictions and hopes, but with the realization that presently only the lead/acid system is commercially available. The bipolar version may reach 50 Wh kg^{-1} energy density, but this is also a prediction. A system that may reach the market soon, and that has gone through the most extensive testing, is the zinc/bromine battery developed originally by EXXON, but brought to the present state of a high pilot production by SEA, in Austria [25]. In the USA, it is represented by POWERCEL Corporation, Boston. This rechargeable battery system combines the three vital 'E's' of energy, environment and economics that have been advocated by Ruetschi [26]. The rechargeable alkaline MnO_2/Zn system may also be a candidate if it proves possible to produce a bipolar, high-current, high-energy design (200 W kg^{-1}, 100 Wh kg^{-1}) that gives 500 cycles. It should be noted, however, that the proposal to use the second-electron discharge in a heterogeneous mode through a soluble Mn(II) species has only very slim chances of succeeding in spite of frequent and widely publicized claims. The need for a large amount of low-density carbon reduces the volume energy density to far less than is presently achievable with the limitations to a part of the one-electron capacity. The solubility of the Mn(II) species cannot be stopped by any low-resistance separator material presently known and its presence on the zinc side, even in traces, causes intolerable corrosion gassing [27].

Summary and outlook

When comparing the rechargeable alkaline MnO_2/Zn battery with other rechargeable systems for the consumer market, it must be remembered that nickel/cadmium and nickel/metal hydride cells face the obstacles of high initial cost (including special chargers) and the need for consumer education in the areas of unreliable shelf life and rapid self-discharge at elevated (e.g., summer) temperatures. This is exactly the situation that has helped primary alkaline MnO_2 batteries secure the largest portion of the consumer market. There is no reason to believe that people object to recharging batteries to save money, but there is proof that they get tired of charging batteries always before they needed them.

There is a widespread opinion that the consumer market will split into the following three sections:

(i) primary and re-usable alkaline MnO_2/Zn batteries; this will represent the largest group of disposable batteries;

(ii) primary and rechargeable lithium batteries for extreme working conditions and highest capacity requirements; these will also cover a sizeable portion of the market, and

(iii) a smaller section that covers the high-power, fast-charging applications for which nickel/cadmium and nickel/metal hydride cells are best suited.

It is interesting that primary cell manufacturers, such as Eveready, Duracell, VARTA and Toshiba have made their choice in aquiring manufacturing positions in the nickel/metal hydride area. As has been the case with primary batteries, the trend to fewer models and types is also strong, leading to the 3-C alliance for the standardization of battery packs and devices [28].

The well-prepared action of the third largest US manufacturer, Rayovac, to introduce re-usable MnO_2/Zn batteries in all primary formats was not been taken seriously until it surfaced in late-1993 with a tremendously effective marketing effort, larger than any other previously made in the rechargeable field, directed to consumers that purchase batteries in supermarkets (40%) [29]. In the first three months of 1994, RENEWAL batteries captured more than 50% of the rechargeable battery market in the USA.

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