

LONG LIFE SEALED NICKEL-ZINC CELL USING A NEW SEPARATOR

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Summary

Because of internal shorting due to zinc (Zn) dendrite formation at the Zn electrode, nickel-zinc (Ni-Zn) secondary cell cycle life is somewhat less than the Ni-Cd cell cycle life. To solve this problem, a new kind of separator was developed which consisted of nylon non-woven cloth coated with poly(vinyl alcohol) (PVA) containing boric acid. This separator has a high ionic conductivity, but is resistant to zincate ion penetration. A large number of additives, effective for Zn dendrite suppression, was also tested. From them, bismuth oxide (Bi_2O_3) was selected and added, together with calcium hydroxide ($\text{Ca}(\text{OH})_2$), to the Zn electrode. A charging method, applying an intermittent anodic pulse, was found to be effective to reduce the Zn electrode shape change and prolong the cycle life of this cell. By using these materials and investigating a cell construction containing an electrolytic solution and hydrogen gas absorber, sizes AA, C, and D sealed Ni-Zn cells were developed whose charging and discharging cycle life achieved over 500 cycles, for a size C cell.

Introduction

The nickel-zinc (Ni-Zn) system is attractive as a secondary cell [1 - 4] because of its high energy density, low material cost, and the low level of pollutants contained in it. Although this system has been studied extensively for electric vehicle applications, it would be a suitable power source for many portable devices if the cell were tightly sealed and had a prolonged life. Its cycle life, however, is less than that for a nickel-cadmium (Ni-Cd) cell because of internal shorting due to Zn dendrite formation and the Zn electrode shape change. An attempt has been made to develop a new sealed, cylindrical Ni-Zn secondary cell. The above problems [5 - 7] have been solved by combinations of a newly developed separator, the Zn electrode composition, a gas absorption electrode and the charging method.

Experimental

Zinc anode

The major factors causing short cycle life in the Ni-Zn cell are shape change and dendrite formation in the Zn electrode, as mentioned previously. During discharge, the Zn electrode dissolves in the alkaline electrolyte solution to form zincate ions, $\text{Zn}(\text{OH})_4^{2-}$ [8, 9]. In the subsequent charging process, zincate ions in the solution deposit on the electrode as Zn metal. This plating process, however, does not proceed uniformly over the entire electrode surface, but is concentrated at the most probable sites. This phenomenon causes the electrode to change shape. At the same time, dendrite formation occurs. To minimize the Zn electrode shape change, dendrite formation, and hydrogen gas evolution, various kinds of additives have been evaluated using a simple 60 mm × 50 mm × 10 mm test cell made from acryl resin plate. The main Zn electrode component is ZnO powder. Polytetrafluoroethylene (PTFE) dispersion is used as a binder. Small PTFE particles together with other components were mixed and rolled to form a 0.35 mm thick sheet. Two of these sheets were pressed, one onto each side of copper expanded metal, to make a Zn electrode. The amount of charge at each cycle was limited to 50% of the theoretical capacity for the Zn electrode which was then introduced into a test cell with the two Ni oxide sheets. The electrolyte was 8N KOH, containing saturated ZnO. Charge and discharge currents were 5 mA/cm².

Nickel cathode

The nickel oxide cathode (NiOOH) was of the sintered type usually used in Ni-Cd cells. Its capacity was 30 mA h/cm² and its thickness was 0.7 mm.

Separator

Many different materials were tested as separators to determine which would obviate Zn dendrite penetration. Of these, it was found that PVA (poly(vinyl alcohol)) film, containing some additives, was the best for this purpose. PVA film itself, however, is mechanically weak and a substrate is needed on which to coat the film. The substrate must be durable in concentrated alkaline solution, thin, porous, and mechanically strong. To this end, several extruded cloths were selected.

PVA film was coated on Dynel, which is a copolymer of acrylonitrile and poly(vinyl chloride), as follows: the PVA concentration of the coating solution was 10%; additions, such as H₃BO₃, MgO, β-Al₂O₃ and TiO₂, were made to the PVA solution. The concentration of the added H₃BO₃ was 1.2%. The concentrations of the other additives were 10%. The solution was coated on each side of the Dynel and dried. To select the best separator additives, the amount of Zn ion penetration through a separator was determined by using an electrolytic cell, as shown in Fig. 1. A constant current of 50 mA/cm² was passed for 3 h between the Zn anode and the Ni cathode

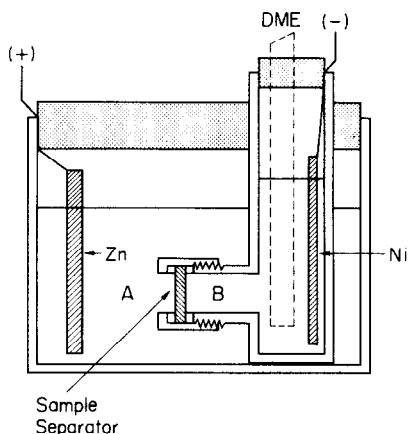


Fig. 1. Electrolytic cell to determine Zn^{2+} penetration quantity: A: 8M KOH + 0.5M ZnO (initial), B: 8M KOH.

for each sample separator examined. The Zn^{2+} ion concentration at site B (Fig. 1), penetrating through the sample separator, was then determined by polarograph.

Electrolyte

Potassium hydroxide (KOH) is favorable because of its high conductivity, especially at low temperatures. To minimize Zn dissolution during discharge, the KOH was saturated with zinc oxide (ZnO). The recommended KOH concentration is greater than 5M. Regulation of the amount of electrolyte in the cell container is a very important factor in attaining long cell life, because dendrite formation largely depends on the amount of electrolyte.

Hydrogen absorption electrode

During the charging process, especially at the final charging stage, dissociation of water in the electrolyte solution is inevitable in cell systems such as the nickel-zinc cell which have a high terminal voltage, giving rise to the evolution of oxygen and hydrogen. Although oxygen is chemically absorbed by the Zn electrode to give ZnO, hydrogen is not absorbed. Thus, the hydrogen gas accumulates in the cell during repeated cycles, resulting in an increase in internal pressure. This problem was solved by the use of a small platinum-catalyzed auxiliary electrode set in the center of the cell.

Results and discussion

Zinc anode

Figure 2 shows the effect of additives on the Zn anode cycle life in the test cell. As seen in curves 1, 4 and 5, bismuth trioxide (Bi_2O_3) addition to the Zn electrode has a greater effect on cycle life improvement than

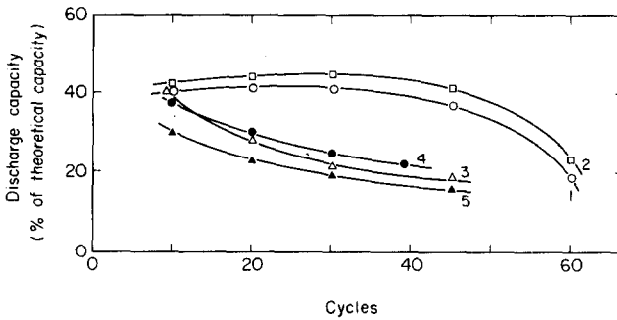


Fig. 2. The effect of additives on zinc anode cycle life in the test cell:

	ZnO	Zn	Bi ₂ O ₃	CdO	HgO	PTFE	Electrolyte
1	85.9	—	9.6	—	—	4.5	} ZnO saturated 8N KOH
2	76.5	9.6	9.6	—	—	4.3	
3	9.6	77.1	9.6	—	—	3.7	
4	85.9	—	—	9.5	—	4.5	
5	90.7	—	—	—	4.8	4.5	

has the addition of cadmium oxide (CdO) or mercury oxide (HgO). The addition of about 10% of Zn powder is also effective (curve 2). Bismuth trioxide is considered to change into Bi metal during the charging process in alkaline solution, which would provide electrode conduction paths. This should reduce the electrode reaction overvoltage and prevent hydrogen evolution in the charging process [6].

The effects of calcium hydroxide (Ca(OH)₂) and electrolyte concentration on the Zn anode cycle life of the test cell were also studied.

As shown in curves 1 and 4 of Fig. 3, a 10% (by weight) approx. Ca(OH)₂ addition is effective in improving cycle life. Calcium hydroxide is considered to inhibit Zn metal dissolution [10, 11]. Therefore, Zn dendrite formation and shape change should be effectively suppressed. The results showed that the Zn anode should consist of ZnO, Zn, Bi₂O₃, Ca(OH)₂ and PTFE.

As these components were mixed and rolled, the PTFE particles changed into three dimensional, complex fibers, which hold the electrode composite tightly. The Zn anode surface is very porous and involves a large surface area, which will reduce the effective current density to suppress dendrite formation and shape change.

As shown in curves 1 and 4 of Fig. 3, the Zn anode cycle life is greater in 4N KOH than it is in 8N KOH. For increased electrolyte conductivity, however, the higher concentration is preferable. A concentration of 8N KOH was adopted, therefore, to obtain a high power battery.

Separators

Figure 4 shows the relative mechanical strength changes for several extruded cloths in 8N KOH solution containing 0.5 M ZnO. Dynel and

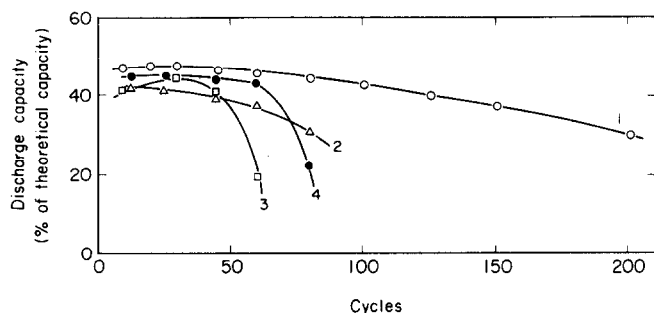


Fig. 3. The effect of additives and electrolyte on zinc anode cycle life:

	ZnO	Zn	Bi ₂ O ₃	Ca(OH) ₂	PTFE	
1	68.5	8.6	8.6	9.4	4.9	ZnO saturated 4N KOH
2	72.5	9.0	9.0	4.8	4.7	
3	76.5	9.6	9.6	—	4.3	ZnO saturated 8N KOH
4	68.5	8.6	8.6	9.4	4.9	

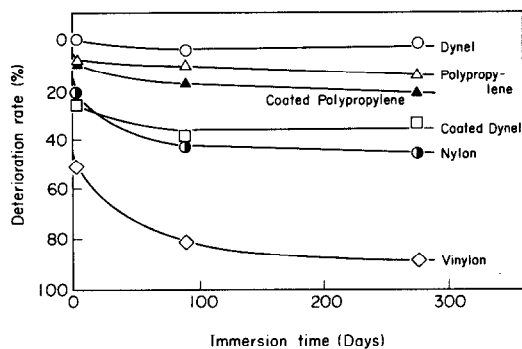


Fig. 4. Relative substratum strength changes in 8N KOH solution.

polypropylene maintain their initial strength for extended periods of time. PVA-coated Dynel and polypropylene are also durable in concentrated KOH solution.

The amount of Zn²⁺ penetration and the electrical resistivity of PVA film containing some additives and coated on each side of a Dynel sheet are listed in Table 1. PVA film containing H₃BO₃ showed the lowest Zn²⁺ penetration [5]. The electrical resistivity of this film is of the same order as that of other films. This should allow the preparation of an excellent separator which would prevent dendrite penetration without decreasing its ionic conductivity. This supposition was confirmed by cycle life evaluation using the test cell, as shown in Fig. 5, where the discharge capacity efficiency changes were reproduced. The electrolyte consisted of 8N KOH containing 0.5M ZnO. Of the several types of PVA film coated on Dynel, PVA film containing H₃BO₃ showed the best performance. In consequence, PVA film containing H₃BO₃, coated on Dynel or polypropylene, was selected as a separator.

TABLE 1

The effect of additives on PVA film separator characteristics

Separator	Zn ²⁺ permeation* (μmol)	Electrical resistance ($\Omega\text{ cm}$)
PVA + H ₃ BO ₃	0.45	67.9
PVA + MgO	2.55	57.1
PVA + β -Al ₂ O ₃	2.85	50.4
PVA + TiO ₂	3.00	69.8

*Concentration at site B in Fig. 1, determined by using polarography after 3 h electrolysis.

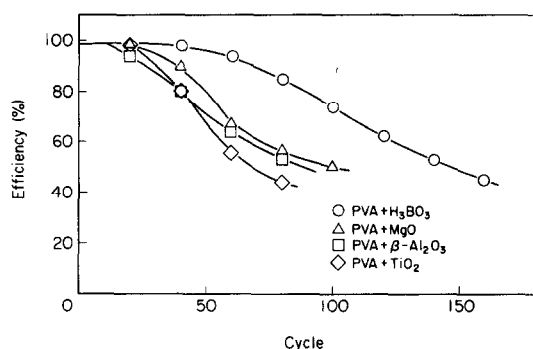


Fig. 5. The effect of the separator on Ni-Zn test cell cycle life.

Separator system and cell construction [5 - 7]

The separator system and sealed cell construction were tested using components selected according to the preceding section. The most important property required of the separator system for the Ni-Zn cell is prevention of dendrite penetration, but it must also be highly ionically conductive, stable in concentrated alkaline solution, resistant to the oxidative action of cathode materials, nickel hydroxide (NiOOH), and, at the same time, it must absorb the electrolyte such that it wets the electrode surfaces and prevents leakage.

Figure 6 shows this system. It consists of three layers: two separator layers, mentioned earlier, and a layer of electrolyte absorber. The latter consists of a relatively thick, extruded polyamide sheet treated in a solution containing a surface-active reagent to increase its electrolyte absorbability. The nature of this layer is also very important with regard to cell performance, especially when cycle life is limited by electrolyte leakage.

The separator system is placed between the Zn anode and the nickel oxide cathode with the separator side facing the Zn anode. They are rolled together to form the electrode system.

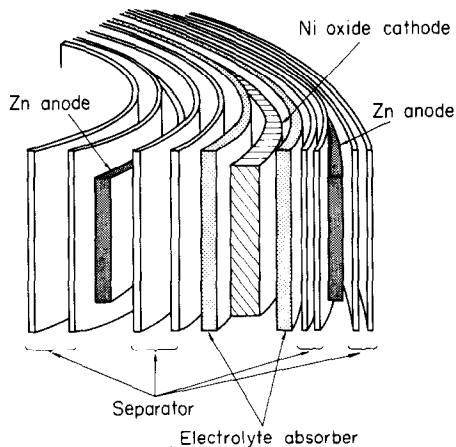


Fig. 6. Separator system structure.

A cross-sectional view of the cell is shown in Fig. 7 (a) and (b). The rolled-up electrode system, with an auxiliary electrode, is inserted into a nickel-plated steel can after being placed in an insulating plastic tube. It is sealed tightly with a plastic cover having a positive terminal and a safety vent to prevent any unexpected internal pressure increase.

The cell capacity is controlled by the capacity of the nickel oxide electrode. The capacity of the Zn electrode is made 2-3 times greater than that of the nickel oxide electrode.

A small auxiliary absorption electrode is set in the center of the cell and is electrically connected to the nickel oxide cathode *via* a diode and a resistor in series. The hydrogen is absorbed and forms water by oxidation. The auxiliary electrode is constructed from a small, sintered nickel plate on which small amounts of Pt and PTFE particles are deposited. Platinum acts as a catalyzer for H_2 oxidation and PTFE prevents the water formed from adhering to the electrode.

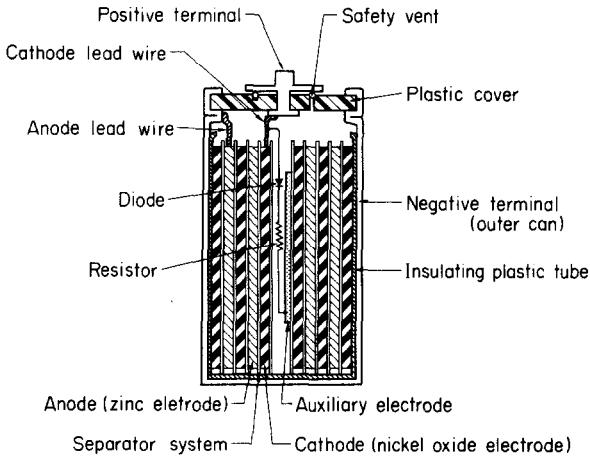
The auxiliary electrode can also be used for other purposes if, as in the case of cell construction (b), it is electrically connected to an isolated terminal (the third electrode terminal). The third electrode terminal is mounted on the plastic cover around the positive terminal (Fig. 7(b)). If the voltage (E_{13}) is monitored between the positive pole and the third electrode terminal, the charging current cut off timing [7] can easily be noted.

Charging and discharging process

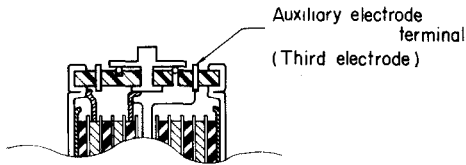
Figure 8 shows the internal pressure change and E_{13} during charge and the following interval.

The internal pressure first shows a plateau: here, H_2 is evolving slowly, but it is absorbed by the auxiliary electrode. When the cell becomes fully charged, a steep pressure increase occurs until charging ceases. This is mainly due to O_2 evolution from the cathode, but the O_2 rapidly oxidises the Zn electrode and, after the charging current is stopped, the pressure almost returns to the initial level.

The voltage, E_{13} , stays almost constant at 0.8 V, while the cell is filled with H_2 only: here, the auxiliary electrode acts as a hydrogen electrode and



(a)



(b)

Fig. 7. Ni-Zn cell cross-sectional view. (a) Two terminal cell; (b) three terminal cell with third electrode.

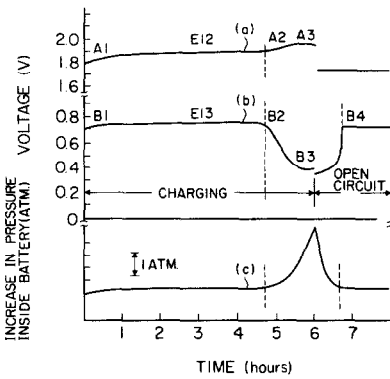


Fig. 8. Cell voltage, E_{13} , and internal pressure changes during charge and intervals. (a) Cell voltage; (b) E_{13} ; (c) internal pressure.

effectively absorbs H_2 . When O_2 begins to evolve, the absorption electrode ceases to function because the Pt catalyzer is oxidized by O_2 and E_{13} begins to fall. The auxiliary electrode does not absorb H_2 until after the O_2 has evolved, when it regains its function. If this voltage reduction is monitored during the charging process therefore, the end point is easily seen; this

voltage change is larger and clearer than that of the cell voltage at that point. If there is no auxiliary electrode within the cell, a gradual pressure increase is observed throughout the charging process.

The cell's internal pressure change with repeated charge-discharge cycles is shown in Fig. 9. When no auxiliary electrode is mounted in the cell, the pressure increase is very large and is almost linear with the number of cycles, as seen in curve (a). The pressure increase is slightly suppressed when the auxiliary electrode is connected to the cathode through a resistor only, as shown in curve (b). Curve (c) shows the case when the absorption electrode is connected to the cathode through a diode: the pressure increase is largely suppressed. A diode and a resistor in series between the auxiliary electrode and the cathode gives the best performance (*i.e.*, the most preferable current regulation for hydrogen absorption), as shown in curve (d).

Three charging modes were tried to determine the best method of improving the cycle life of the Ni-Zn cell. These procedures are shown in Fig. 10.

The first method was that used for the standard cycle test. Constant current is applied for a constant time or until the cell voltage attains a definite value. It is difficult using this method to avoid overcharge or undercharge.

The second procedure was a three wire method applicable to category (b) cell construction of Fig. 7, using the H₂ absorption electrode as the third electrode discussed above. Constant current is applied until O₂ starts to

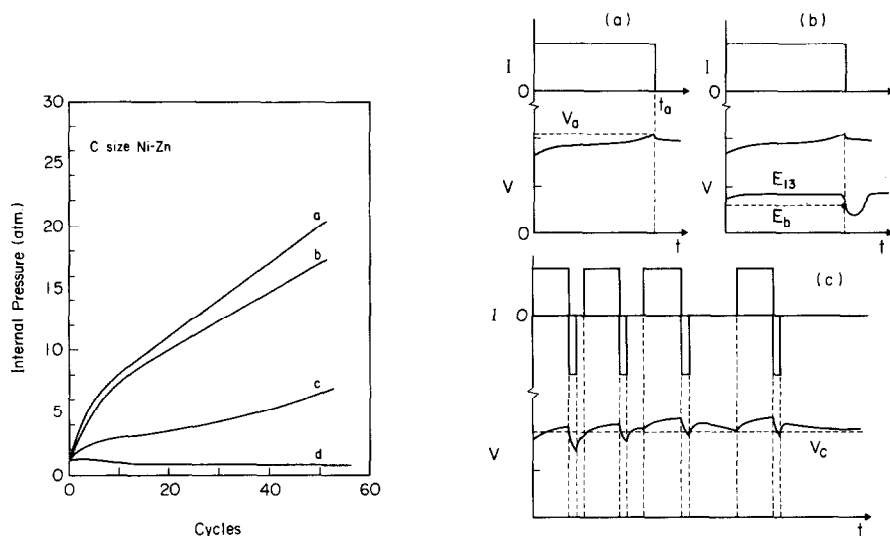


Fig. 9. Internal pressure change with cycles for C-size Ni-Zn cell. (a) Without absorption electrode (A.E.); (b) A.E. + resistor; (c) A.E. + diode; (d) A.E. + resistor + diode.

Fig. 10. Charging modes for Ni-Zn cell. (a) Ordinary method, V_a : cut off voltage; (b) three-wire method, E_b : cut off voltage of E_{13} ; (c) open circuit voltage sensing method (two wire method), V_c : open circuit voltage.

evolve in the cell. Charging current cutoff timing is determined by voltage value E_{13} .

The third method (the two wire method), is applicable to both types of cell (Fig. 7) in which changes in the cell's open circuit voltage (OCV) with charge state are monitored. The important feature of this method is to have a short discharge process between the pulsating charge and the open circuit voltage sensing process. This discharge process makes the following cell OCV settle down in a shorter time to a stable value. If the OCV is lower than a predetermined value, corresponding to 100% charge state, the next charge pulse starts. In addition, the discharge pulse seems to quickly dissolve Zn dendrites formed by the charging process. This process, therefore, effectively reduces the Zn anode shape change, as shown in Fig. 11. Two large rectangles in Fig. 11 indicate a Zn anode divided into 16 equal sections. The figures in each section show its weight as a percentage of the average value. Figure 11(a) shows the weight change (which can be equated to the shape change) after 140 charging cycles using the ordinary charging method. Note that the Zn is concentrated in the center portion of the electrode by the repeated cycles. The coefficient of variation, $3\sigma/\bar{x}$, for these weight changes attains over 100% at 140 cycles. By contrast, as shown in (b), the OCV sensing method effectively suppresses shape change. The variation coefficient is under 40%, even after 200 cycles.

The three wire method is elegant, but the cell construction is rather complicated and the cell construction process is troublesome. Therefore,

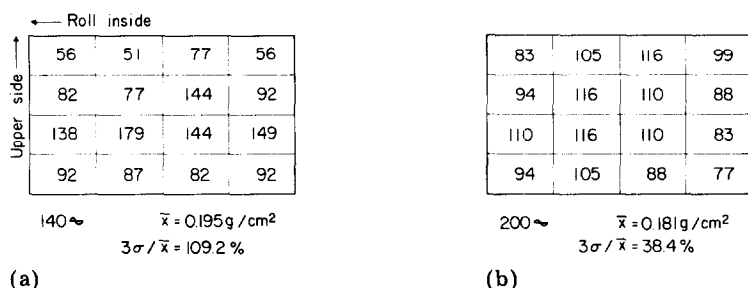


Fig. 11. Zinc electrode shape change with charge-discharge cycles for size C cell. (a) Ordinary charging method with 300 mA constant current; (b) open circuit sensing method (two wire method).

the two wire method is considered to be the best for the Ni-Zn secondary cell in the present case.

Performance

Three kinds of Ni-Zn, sealed, cylindrical cells, sizes "D", "C" and "AA", were constructed. The characteristics for each size are shown in Table 2.

TABLE 2
Specifications for Ni-Zn cells

Term		Size		
		AA	C	D
Cell voltage	(V)	1.6	1.6	1.6
Capacity	(A h)	0.45	1.5	3.5
Height	(mm)	49	49	60
Diameter	(mm)	14	25	33
Weight	(g)	20	65	125
Power*	(W)	0.6	2.3	5.4
Power density*	(W/kg)	32	36	44
Energy density**	(W h/kg)	26	32	40
Preferable maximum current on continuous discharge	(A)	0.15	1.5	3.5

*Measured by 1C discharge.

**1 V cutoff.

The advantages of these cells are:

- (i) higher working voltage, (1.6 V) than Ni-Cd cells (~ 1.2 V);
- (ii) lower weight by 20% than corresponding size Ni-Cd cells;
- (iii) high energy density;
- (iv) able to *withstand* relatively high discharge rates;
- (v) flat discharge characteristics.

To clarify the Ni-Zn cell features, 600 mA discharge characteristics for the several kinds of C size cells at 25 °C are shown in Fig. 12. The capac-

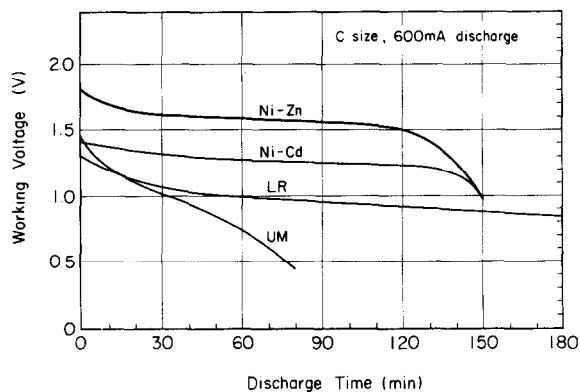


Fig. 12. Discharge curves for several kinds of size C cells where the discharge current is 600 mA at 25 °C.

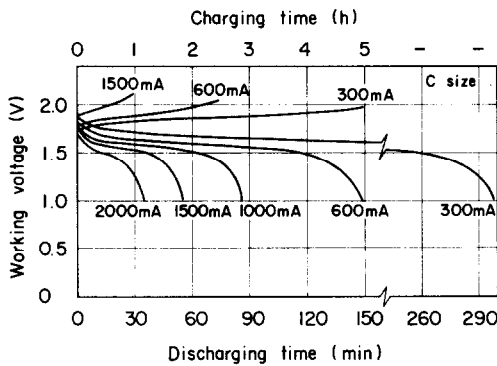


Fig. 13. Typical continuous charge-discharge curves for constant currents at 25 °C. Size C cell.

ities of the Ni-Zn and Ni-Cd cells are 1.5 A h, but, as can be seen, the working voltage for the Ni-Zn cell is higher, by about 0.4 V, than that for the Ni-Cd cell. It is 0.6 V higher than that for an alkaline cell (LR) and is 0.7 V higher than that for a conventional carbon-zinc cell (UM).

Typical continuous charge-discharge curves for constant currents at 25 °C are shown in Fig. 13 for a size C cell. The amount of electricity for the charging process is 1.5 A h at each current. High-rate 1500 mA charging (1 C) is possible, as seen in the Figure and the working voltage is acceptably flat during discharge. The difference in working voltages due to the discharge rate is fairly small, although discharge efficiency begins to decrease when the discharge current exceeds 1500 mA (1 C).

The amount of charge capacity retention during storage was examined. Figure 14 shows it to have decreased to 70% of the initial amount after 1 month at 25 °C. It was proved to be associated with self-discharge of the nickel oxide cathode.

Figure 15 shows the cycle life for a size C Ni-Zn cell using two different charging methods. The OCV sensing method is superior to the ordinary

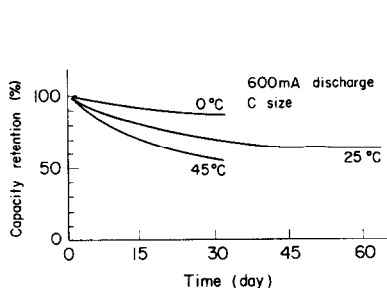


Fig. 14. Size C cell capacity retention during storage. Data obtained with a 600 mA discharge.

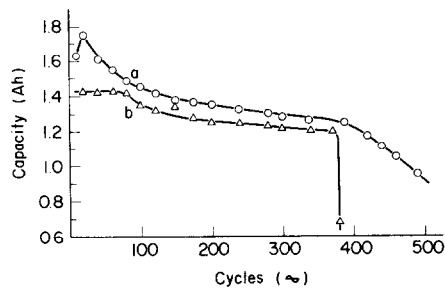


Fig. 15. Discharge capacity changes for size C Ni-Zn cell with cycles. (a) Continuous charging using 300 mA constant current; (b) open circuit voltage sensing method (two wire method).

method although 350 cycles were attained by each. By using the OCV sensing method, 500 cycles are possible before the cell capacity decreases to 60% of nominal.

Conclusion

A long life, sealed, cylindrical Ni-Zn secondary cell was developed by combining various new materials and techniques such as:

(i) a PVA separator film containing H_3BO_3 coated on a thin extruded cloth, which can effectively suppress zinc metal dendrite penetration;

(ii) zinc electrode made from ZnO , Zn , Bi_2O_3 , and $Ca(OH)_2$ powders and PTFE dispersion, which is porous and has a large surface area;

(iii) electrochemical oxidation of hydrogen gas by an auxiliary electrode, which prevents the battery from swelling or leaking;

(iv) development of two charging methods which completely avoid overcharge.

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