# SOME ASPECTS OF SEALED NICKEL CADMIUM CELLS

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Sealed Nickel Cadmium Cell System is termed till today as the most reliable power pack for electronic apparatus, specially in low temperature use. This paper brings out the development and production of sealed nickel cadmium cells of pocket plate construction. The author who has gained reputed experience in production of *Ni-Cd* cells in East Germany, discusses also the Major problems faced by the battery manufactures of to-day.

In 1899, Jungner[1], discovered and took patents on *Ni-Cd* cells. Since then a considerable work has been directed in order to explain the phenomenon related to *Ni-Cd* system. During these experimentations several important properties of *Ni-Cd* cells have been brought to light. But till today, the different types of reactions which occur in positive and negative plates of a *Ni-Cd* cell, during charging and discharging, have not been fully explained. The most modern development is sealed type cells. When one studies the reactions in a vented *Ni-Cd* cell, it seems impossible to operate it in a hermetically sealed system. That is why a study of the development of sealed *Ni-Cd* cells is very interesting.

In order to understand the development of a sealed system, it is worthwhile to note the chemical reactions in an ordinary vented type cell during charging and discharging. In an ordinary *Ni-Cd* cell of pocket plate construction, the positive plate is of $Ni\,(OH)_2$ with powdered graphite and negative plate is of $Cd\,(OH)_2$ with powdered iron. The two plates are separated by a porous non-metallic separator. The electrolyte is KOH of density $1{\cdot}20$—$1{\cdot}30$ $gm/cm^3$. It has been generally agreed that during charging the positive electrode undergoes oxidation and the negative reduction. During discharging the positive electrode undergoes reduction and the negative, oxidation. The transfer of oxygen (or hydroxyl-ion) is carried out by the electrolyte and the electrolyte nearly does not take part in the chemical reactions occurring in positive and negative plates during charging and discharging.

A close study of the reactions occuring in positive and negative electrodes during charging and discharging reveals that :

(*a*) Positive electrode

$$2\,Ni\,(OH)_2 + 2\,OH \underset{\text{Discharge}}{\overset{\text{Charging}}{\rightleftarrows}} 2\,Ni\,O\,(OH) + 2\,H_2O + 2\,\mathrm{e} \qquad (1)$$

Glemser and Einerhand[2] believed that during charging first $NiO_2 \times H_2O$ is formed which is a very unstable compound. Therefore it immediately reacts with $Ni\,(OH)_2$ to form $NiO\,(OH)$. This reaction is purely chemical in nature and, therefore, no extra charge is necessary for this chemical reaction.

During discharging, $NiO\,(OH)$ is first reduced thus :

$$2\,Ni\,O\,(OH) + Ni\,(OH)_2 \rightarrow Ni_3\,O_2\,(OH)_4 \qquad (2)$$

$Ni_3\,O_2\,(OH)_4$ is then further reduced thus :

$$Ni_3\,O_2\,(OH)_4 + 2\,H^+ + 2\,e \rightarrow 3\;Ni\;(OH)_2 \qquad (3)$$

Glemser & Einerhand[2] have shown that (2) and (3) give rise to a two-step discharge characteristic curve for the positive plate as shown in Fig. 1.

Other scientists headed by Falk[3] believe that during charging, $NiO_2$ is not at all formed atthe positive electrode and that only $\beta\ NiO\ (OH)$ is produced. Falk[3] could not find traces of $Ni_3\,O_2\,(OH)_4$ during discharging of the positive plate by X-ray investigation and, therefore, opined that the step characteristic of positive electrode is not due to the formation of $Ni_3O_2\,(OH)_4$ given by (2) and (3), but by oxygen absorbed by the $Ni\,(OH)_2$.

(*b*) Negative electrode

$$Cd\,(OH)_2 + 2\,e \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftarrows}} Cd + 2\,OH \qquad (4)$$

Therefore, the total reactions in a *Ni-Cd* system is obtained by summation of (1) and (4)

$$2\,Ni\,(OH)_2 + Cd\,(OH)_2 \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftarrows}} 2\,Ni\,O\,(OH) + Cd + 2\,H_2\,O \qquad (5)$$

Let us now find out the emf of a fully charged *Ni-Cd* system. In this case the chemical reactions given by (1) and (4) are written in a slightly modified form as shown below :

$$\overset{\text{Reduction}}{\underset{\text{solid}}{Ni\;(OH)_2}} + 2\,(OH)^- \rightarrow \underset{\text{solid}}{Ni\,O_2} + 2\,H_2\,O + \overset{\text{Oxidation}}{0{\cdot}49\ V} \qquad (6)$$

$$\underset{\text{solid}}{Cd} + 2\,OH^- \rightarrow \underset{\text{solid}}{Cd\;(OH)_2} - 0{\cdot}815\ \text{V} \qquad (7)$$

Substracting (7) from (6) and rearranging we get :

$$Ni(OH)_2 + Cd\,(OH)_2 \rightarrow Ni\,O_2 + Cd + 2\,H_2\,O + 1{\cdot}305\ V \qquad (8)$$

(8) shows that at the end of charging, the e.m.f. at the terminals will be approximately 1·305V.

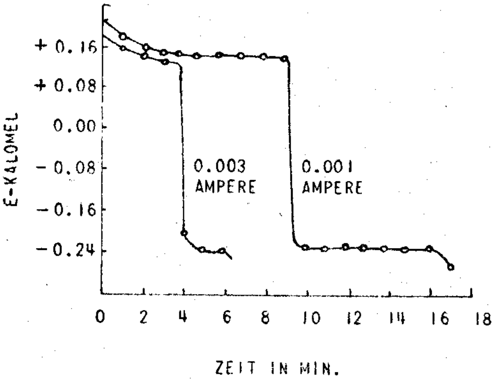


Fig. 1—Discharge characterisctic of β—$NiO\,(OH)$ at different rates of discharge.

As the charging of a *Ni-Cd* cell proceeds, the reactions in positive and negative plates are slightly different :

In the positive electrode

$$2\,(OH) \rightarrow {}^{1}/_{2}O_2\uparrow + H_2\,O + 2e \tag{9}$$

In the negative electrode

$$2\,H_2\,O + 2\,e \rightarrow 2\,(OH) + H_2\uparrow \tag{10}$$

It is observed from (9) that $O_2$ is evolved during charging of the positive plate. It is also seen practically that when a cell is charged to approx. 60 per cent of the nominal ampere hour capacity, $O_2$ is evolved at the positive electrode. When the cell is charged to 90—95 per cent of the nominal ampere hour capacity, $H_2$ is evolved at the negative electrode which can be explained by (10). As the cell is overcharged, $O_2$ and $H_2$ are both evolved more and more. For vented type cells these gases are automatically expelled and, therefore, a considerable loss of charge occurs. That is why a vented type cell shall be charged to 150—160 per cent of the nominal ampere hour capacity in order to get a 100 per cent capacity discharge from the cells. Fig. 2 shows charge and discharge characteristics of a vented type *Ni-Cd* cell of pocket plate construction.

The discovery that $O_2$ at the positive electrode and $H_2$ at the negative electrode could be recombined to get back $H_2O$ led to the development of a sealed Ni-Cd system. Many attempts have been made to bring a recombination of these gases in a cell by using :

(*a*) An electrically heated platinum wire in the cell as patented by Edision[4].

(*b*) A special auxiliary electrode in the cell as patented by Tichenor[4].

These methods were, however, only partially successful. In 1938, Large, etc. found that all the $O_2$ evolved at the positive electrode during charging was not expelled through the vent plugs of cells, but a greater part of it was absorbed at the positive electrode

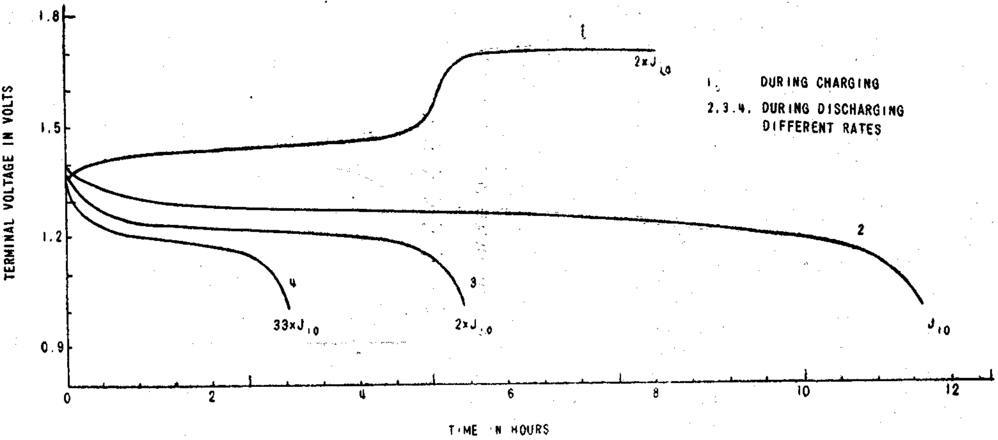


Fig. 2—Charge and discharge characteristics of a *Ni-Cd* vented type cell of pocket plate construction.

This $O_2$ could be utilised to react with already reduced *Cd* of the negative plate to form *Cd* $(OH)_2$. That is why a vented *Ni-Cd* cell, when discharged immediately after full charge, gives better capacity than that obtained from the same cell after a few hours of storage before discharge. But $H_2$ evolved at negative plate can never be employed successfully. This theory led to the development of a sealed *Ni-Cd* system. However, lack of suitable separator material delayed its production. Finally in 1948, New-mann[4] of the Bureaude Technique Gantrat filed two patents covering the following three most salient requirements in a sealed *Ni-Cd* system: (*a*) an excess of negative active material (*b*) a minimum of electrolyte and (*c*) a gas permeable separator.

### *Excess of nagative active material*

Let us now discuss in more details the use of excess negative active material in sealed *Ni-Cd* cells.

It has been already stated that when a cell is charged approximately 60 per cent of the rated capacity, $O_2$ is evolved. $H_2$ is not evolved till the charging of negative plate is 90—95 per cent of the capacity of negative plate. If positive and negative plates of similar capacity are used in a cell, $H_2$ is evolved when the cell is almost fully charged. This evolution of $H_2$ is not desirable as already explained. But if a negative plate having a charge acceptance capacity of 50—70 per cent more than that of the positive plate is used to make a sealed cell, on charging the same (the positive and negative plates are separately formed before assembly) only $O_2$ is evolved and not $H_2$ at any stage of charging. When the cell is over-charged, $O_2$ of the positive plate reacts with already reduced *Cd* of the negative plate forming *Cd* $(OH)_2$. Therefore, the negative plate is never fully charged; instead a reserve negative active material is invariably found in it (Fig 3). As a result, the end voltage on charge of a sealed cell always remains constant even if the cell is over-charged Fig 4. and Fig5 illustrates the discharge characteristics of a sealed button cell.

### *Minimum of electrolyte*

Let us calculate the quantity of electrolyte required for a satisfactory functioning of a sealed Nickel-Cadmium cell[5]. Consider a sample cell (see Fig. 6) for this purpose.

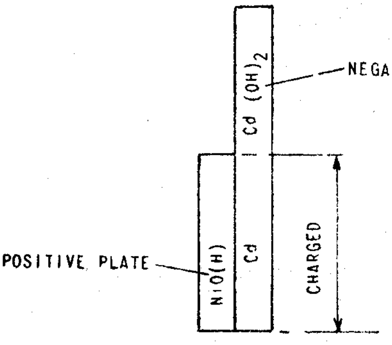


Fig. 3—Reserve Cd (OH) 2 in negative plate.

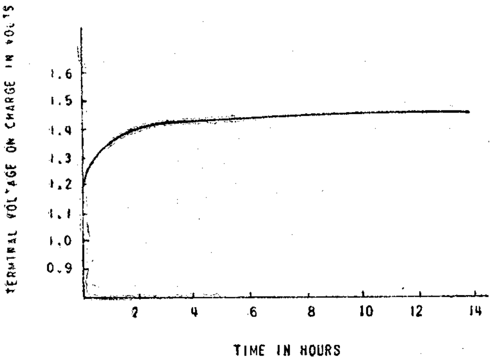


Fig. 4—Terminal voltage during charging of a sealed button cell at 10 hour rate.

Let $E$ = thickness of electrodes (positive) in mm

$e$ = mean distance between two electrodes in mm

$\pi$ = capacity of electrode (positive)/vol *i.e.* in Ah/mm$^3$

$\alpha$ = electrolyte volume/capacity of positive electrode in mm$^3$/Ah

$k$ = porosity factor for separator.

Then

$$\frac{e}{E} = \frac{\alpha \; \pi}{2 \; k} \tag{11}$$

'$k$' is given by :

$$k = \frac{V_T - V_S}{V_T} \tag{12}$$

where $V_T$ = Volume in between positive and negative electrodes in mm$^3$

$V_s$ = Volume of separator material in mm$^3$.

When density of separator material is '$D$' and weight of the separator is '$W$' then

$$V_S = W/D \text{ mm}^3 \tag{13}$$

and

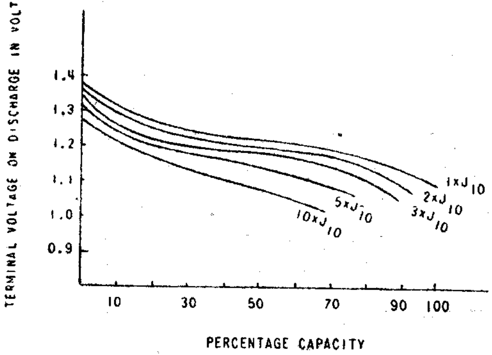
$$k = \frac{V_T - W/D}{V_T}$$

(11) and (13) give the minimum quantity of electrolyte required in a sealed cell.

*Separator material*

A good separator material in a *Ni-Cd* system should be :

(*a*) A very good absorber of electrolyte (*i.e.* $KOH$). It has been already shown that a minimum quantity of electrolyte is required for a proper functioning of *Ni-Cd* sealed cell. Therefore, the separator used in the cell must absorb the electrolyte required for the cell. If by any chance, there is an excess of electrolyte in the cell in the form of liquid, it may partly or completely submerge the negative plate, and thereby prevent $O_2$ evolved at the positive plate during charging of sealed cell, to react with $Cd$ of the negative electrode. Thus, $O_2$ is not absorbed and if prolonged overcharge is continued $H_2$ may be evolved. The pressure due to $O_2$ and $H_2$ may increase to cause a rupture of the cell's body.



g. 5—Discharge characteristics of a sealed button cell at different rates of cdischarges.

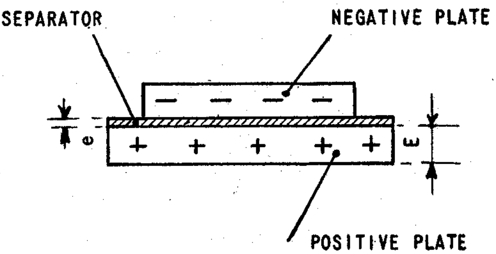


Fig. 6—A sample cell

(*b*) perfectly non-reactive with $KOH$ of the cell

(*c*) gas permeable; should also have no reaction with $O_2$ & $H_2$

(*d*) durable and sufficiently tough

(*e*) able to withstand sufficiently high temperatures.

These qualities can best be seen in woven nylon cloth and, therefore, it has been accepted as the standard material for separator in sealed *Ni-Cd* cells.

## *Ni-Cd* SEALED CELLS

At present three types of *Ni-Cd* sealed cells are produced :- (*a*) Button cells (*b*) Rectangular cells, (*c*) Pentorch cells. Fig 7 shows different types of 'Button' and 'Rectangular' sealed cells manufactured by Grubenlampenwerke-Zwickan GDR. These cells can use sintered plates or pocket plates. Let us discuss the construction of a button type sealed *Ni-Cd* cell of pocket plate construction (Fig 8) manufactured by Grubenlampenwerke Zwickan GDR.

### *Button cells*

A normal button cell has the following parts : (*i*) positive electrode—$Ni\ (OH)_2$ with graphite and a little quantity of cadmium is used as the active material for the positive plate. The reason why graphite is used with $Ni\ (OH)_2$ is that $Ni\ (OH)_2$ has very high internal resistance and the use of graphite in $Ni\ (O_H)_2$ brings down the internal resistance

Fig. 7—Button and Rectangular sealed cells.

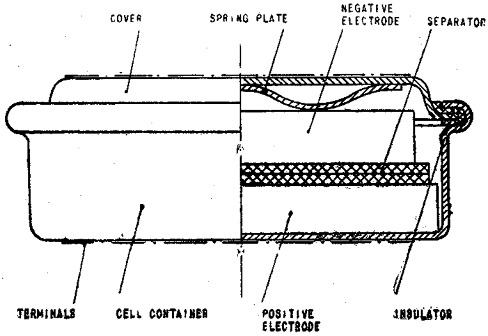


Fig. 8—Internal construction of a sealed button cell.

of the positive plate to a very low value. The internal resistance of a *Ni-Cd* system should always be very low so that higher currents could be drawn from the cell causing a very slight internal voltage drop.

(*i*) *Mode of manufacture*—Powdered $Ni\,(OH)_2$ with powdered graphite is pressed by an automatic press into round buttons. Nickel wire mesh is used under pressure to enclose the button. When two or more positive plates are used in a cell, nickel lugs are spot-welded over the nickel wire mesh.

(*ii*) *Negative electrode*—Powdered $Cd\ (OH)_2$ with $Ni$ powder is used as the negative active material. $Ni$ in the metallic state definitely increases the conductivity of $Cd\ (OH)_2$ but $Cd\ (OH)_2$ itself is a very good electrical conductor. Modern research goes to show that if powdered $Cd\ (OH)_2$ alone is used as the negative active material, during charge and discharge cycles, fine $Ca\ (OH)_2$ particles tend to combine into a bigger mass and thereby the surface area decreases. This gives rise to an increase of internal resistance of the negative plate. When $Ni$ powder is used, it practically acts as a boundary wall between $Cd\ (OH)_2$ particles and thereby prevents fine $Cd\ (OH)_2$ particles to combine into a bigger mass.

*Mode of manufacture*—As in the case of positive electrode, powdered $Od\ (OH)_2$ with Ni powder is pressed by an automatic press into round buttons. Fine Nickel wire mesh is used under pressure to enclose the button. When two or more negative plates are used in the cell, nickel lugs are spot welded over nickel wire mesh.

(*iii*) *Separator*—Woven nylon cloth is used as the separator.

(*iv*) *Cell body*—Nickel plated steel containers are used for housing the cells.

## FORMATION OF CELLS

*Vented type cell*—In the case of vented type *Ni-Cd* cell, the positive and negative plates are assembled in the cell container; proper separator is used in between the two plates of opposite polarity; the cell is charged after pouring in the electrolyte and discharged before it is sold. But in case of sealed cells, positive plates and negative plates may be separately formed before assembly. During formation period, positive and negative plates are charged and discharged separately against standard electrode in polysterene case containing excess electrolyte. Both these positive and negative electrodes (buttons) are fully discharged before assembly.

*Ni-Cd button cell*—The positive electrode fully discharged is placed directly in touch with the bottom of the cell container. Single or double layer of separator, wet with *KOH* of density 1·20—1·30 $g_m/c_m^3$, is placed over the positive plate. Then negative electrode fully discharged is placed over the separator. A spring plate is then put on the negative button electrode and the cover is placed over it. The cell is finally sealed with non-metallic insulator under pressure. Thus a sealed nickel cadmium button cell is formed as shown in Fig 8.

## CELL FAILURES

Although sealed *Ni-Cd* cells have more advantages than disadvantages, yet these disadvantages cannot be totally ignored and modern research is directed to eliminate them. Therefore a detailed mention of the major problems in a sealed cell is very necessary.

The essential problems are :

(*a*) *Difficulty in sealing*—The difficulty in perfectly sealing a cell is very common among the battery manufacturers. When the cell is not fully sealed, $O_2$ evolved at the positive electrode during charging leaks .out Thus, when the cell is overcharged, $H_2$ evolved at the negative plate also leaks out. These $O_2$ and $H_2$ are formed by the electrolysis of $H_2O$ of the electrolyte. Therefore, the cell rapidly losses. $H_2O$ of the electrolyte and gets dried up. This cell cannot be discharged as the internal resistance of the cell is very high. This type of failure is very common and is termed as "Failed open" category[6].

(*b*) *Higher self-discharge in sealed cells*—The self-discharge in a *Ni-Cd* cell is due to two major factors : (*i*) the major portion of $O_2$ evolved at the positive electrode during charging invariably reacts with *Cd* of the negative electrode. However, a considerable part of it is absorbed in the positive electrode or electrolyte. When a sealed *Ni-Cd* cell is stored after a full charge, the $O_2$ absorbed at the positive electrode oxidises the *Cd* of the negative electrode and thereby makes the negative plates less negative and for the positive electrode becomes less positive. Therefore, this chemical reaction during open circuit storage of a cell causes a self-discharge of the order of 25—30 per cent of the rated capacity of the cell. This self-discharge occurs within a very short time. (*ii*) This is due to the local action in a sealed cell. Due to the factor sealed cells, specially smaller ones, have much higher self-discharge than the vented type. Fig 9. gives a self-discharge curve of a DEAC Button cell[7]. In a sealed cell a thin deposit of *KOH* is always seen at the joints in between the inner cell container and the top lid. Therefore, a small current always passes from positive electrode to the negative electrode through this thin layer of (*KOH*) electrolyte. $H_2$ and $O_2$ are evolved. $O_2$ always reacts with negative electrode, but $H_2$ is collected in the cell. Thereby exerting pressure it may become sufficient

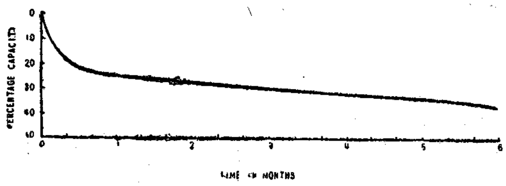


Fig. 9—Selfd ischarge curve for a DEEC cell.

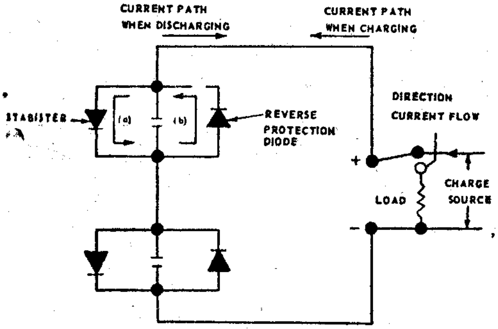


Fig. 10—Stabistor operating circuit used with a nickel cadmium battery : (*a*) current path during change when cell becomes fully charged, (*b*) current path when all is exhausted during discharge.

to cause a rupture of the cell. Although modern research shows that $H_2$ collected inside the cell polarises the positive electrode and the leakage current reduces, yet the self-discharge already taken place before polarisation is quite considerable. Although self-discharge due to this factor is very high in case of smaller cells, it is considerably reduced by using better insulator in between the cell container and the top lid. In the case of vented type cells, self-discharge due to this factor is almost negligible.

(c) *Reversal of polarity when a number of sealed cells are used in series*—During discharge of a battery, one or more cells quickly discharge. The discharge current from the cells charges these faulty cells in reversed polarity[8]. This makes the battery unserviceable within a very short time. However, germanium diodes can be used in parallel with each cell to stop cell reversals (as shown in Fig 10) but this makes the battery very costly and, therefore, cheaper methods should be explored.

## DISCUSSION AND CONCLUSION

Sealed *Ni-Cd* cell is considered to be the most reliable power pack for electronic apparatus, particularly for use at low temperatures. These cells can be overcharged or over-discharged for a long time without causing any injury to the cell. Being sealed, these cells lose no water of electrolyte and, therefore, regular electrolyte checking is unnecessary. There is no risk of the evolution of corrosive spray during periods of over charge and the concentration of *KOH* electrolyte remains practically invarient. Also since no space is required for free electrolyte, the electrode groups can be enlarged to fill almost the whole of the cell container thereby giving a higher output per unit of cell volume.

It is worthwhile, however, to note that the advantages in the sealed Ni-Cd cell more than offset the defects in it and that is why the sealed system has become so popular in the scientific world.

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## REFERENCES

1. Jungner, W., Swedish "Patent No. 10177 dated 11 March, 1899" and "Patent No. 11487 dated 23 Oct. 1899".
2. Glemser, V.O. & Einerhand, J., "Die Chemischen vorgange an der Nickel hydroxydansde des Edisonakkumulators" (ausudem Institute fur anorganische chemic end Elektrochemic der Rheinisch Westfalisch Technischen Hochschule Aachen Eingegangen em) Aug., 1949.
3. Falk, S.V., & Jungner, A.B., paper entitled "Investigation on the Reaction Mechanism of the Nickel Cadmium Cell"(Presented at Columbus Meeting) Oct., 1959.

4. LUMN, H.B. & PARKER, J., "Reactions in Sealed Nickel Cadmium Cells", *Proc. Fourth Intirnat, Symp.,* Brighton (Pergamen Press, London) 1964, p. t29.

5. WEIBER, H.L., Patent No. 1160908 dated 9 Jan., 1964 on "Alkalischer Akkumulator, inbesondere fur rasche Enladungen"

6. E.B. Cuph of Eagle Pitcher Co— "Sealed *Ni-Cd* Batteries" 17th Annual Power Sources conference PSC Public Committee 21—23 May 1963, P. 105

7. "Gasdichte Nickel Cadmium Akkumulator" (Knopf Zallen) a catalogue Published by DEAC Ltd, W. Germany.

8. Subramenyam, C.G. Saha, P.K. & Rao B.R.V. "Some Aspects of Ag-Zn cells" Def. Sc. J., 16 (1966), p. 116.

9. From an unpublished paper "Selbstent ladung in gas dichte Zellen" by Herr Akermann and Her Schwake of GEB Grubenlampen—werke—Zweckau, GDR.