ELECTROLYTE FILL QUANTITY AND LIMITING CAPACITY IN SEALED NICKEL–CADMIUM CELLS

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Summary

An electrolyte management model has been developed to facilitate the evaluation of electrolyte volume and concentration during nickel-cadmium cell operation. The model calculates the optimum electrolyte quantity for filling sealed cells taking into account the maximum volume of a charged cell to prevent oxygen pressure buildup and the influence of charging during formation on electrolyte concentration. Upper and lower limits of electrolyte quantities, and their corresponding effects on cell performance, are also taken into account when deriving the model.

Introduction

Sealed nickel–cadmium cells have the advantage of many years of maintenance-free operation. This is possible due to oxygen recombination mechanism on the negative electrode and suitable electrolyte management [1]. Oxygen is mostly generated on the positive electrode during overcharge, when the active material has reached its final state of oxidation and diffuses through the electrolyte [2]. It then recombines with the negative active charged material preventing its accumulation and pressure buildup [3]. When there is too much electrolyte, as in a flooded cell, there is a high resistance to oxygen transport. Oxygen gas then accumulates, causing a high cell pressure which is eventually released through the cell's safety vent [4].

The amount of electrolyte may vary within a relatively narrow range. At the upper end of the range, the electrolyte volume is generally 95 ± 3% of the free volume. This highest recommended ratio varies to a certain degree as a function of the operating temperature and the charge current. Operation

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at low temperatures or at high overcharge currents requires less electrolyte [5]. On the other hand, at the lower end of the range, there must be sufficient electrolyte to prevent the separator from drying out. This will create a high resistance and a large voltage drop which reduces the cell capacity. Reduced capacity caused by insufficient electrolyte is felt when only about 70% of the separator is filled. Excessive active material loading will also reduce the free volume available for electrolyte and thus lower the available cell capacity [6].

In a sealed cell the negative electrode is deliberately charged more than the positive electrode. This excess charge is required for oxygen recombination to reduce pressure buildup and to minimize capacity fading during cycling. The excess negative capacity is produced in a formation process of the negative electrodes or by repeated cycling of the assembled cell. If the formation process is carried out in the cell, then the electrolyte is usually added when the positive and negative electrodes are discharged. When the cell is then charged during the formation process the electrolyte volume and concentration is changed. Thus, it is useful to know the required electrolyte volume in the discharged state which will result in an optimal fill ratio in the finished product [7].

The purpose of this work is to evaluate the necessary electrolyte fill volume, so that oxygen transfer is not restricted, and to predict the cell capacity for a given loading level of active material.

Water–KOH balance

The electrolyte in nickel–cadmium cells consists primarily of water and a base such as potassium hydroxide (KOH). Conservation of the mass of water and base between the charged and discharged states for KOH requires that:

$$D_c V_c W_c = DVW + \Sigma K_i C_i \tag{1}$$

and for water that:

$$D_c V_c (1 - W_c) = DV(1 - W) + \Sigma H_i C_i \tag{2}$$

The left side of eqns. (1) and (2) represent the amount of base or water, respectively, in the charged cell. The right side is the amount of water or base in the discharged state. The summation terms evaluate the amount of change due to reactions. The index i denotes the appropriate coefficients of the corresponding charge or discharge processes taking place between the two states. These coefficients result from the corresponding electrochemical reactions which occur in the cell during that process. Details of these electrochemical processes as well as water and base release coefficients H_i and K_i for various reactions are evaluated in the Appendix and are summarized in Table 1.

TABLE 1

Water and KOH release coefficients (g/A h) for various reactions

Coefficient	Reactions					
	Charge	Discharge	Overcharge open cell	Overcharge closed cell	Normal overdischarge	Deep overdischarge
i	1	2	3	4	5	6
H_i	0.712	−0.712	0.336	0	−0.672	−0.336
K_i	−0.0978	0.0978	0	0	0	0

Equations (1) and (2) can now be rearranged for the electrolyte concentration in a charged cell as a function of its concentration in the discharged cell:

$$W_c = \{W + \Sigma K_i C_i/(DV)\}/\{1 + \Sigma(H_i + K_i)C_i/(DV)\} \tag{3}$$

This equation is a generalized modification of the one derived by Halpert [7] for a specific reaction only. The electrolyte volume in a charged cell as a function of its volume in a discharged cell:

$$V_c = VD\{1 + \Sigma(H_i + K_i)C_i/(DV)\}/D_c \tag{4}$$

Equations (3) and (4) require the electrolyte density variation as a function of the concentration so that changes in electrolyte concentration and volume may be computed. Electrolyte concentration in nickel–cadmium cells is in the range 0.18 to 0.40 ratio by weight. The density variation at 20 °C in this range of concentration is tabulated in ref. 8. To simplify the preceding calculations a linear relationship between the electrolyte density and the concentration has been assumed. Figure 1 shows a correlation coefficient of 0.9997 with the density varying according to:
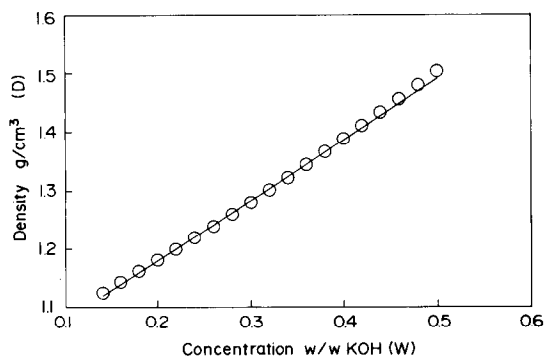
$$D = 0.9741 + 1.031W \tag{5}$$

Fig. 1. KOH electrolyte density at 20 °C.

Similarly, the density variation resulting from concentration changes is given by:

$$D_c = D + b(W_c - W) \tag{6}$$

where $b = 1.031$ g/cm^3.

Equations (3) and (4) were evaluated for a specific capacity (C_i/DV) in the range of 0 - 0.5 A h/g initial electrolyte weight. This range is common for sealed nickel–cadmium cells which undergo the various reactions detailed in Table 1. The dependence of electrolyte concentration and volume on the specific charge input, during various charge or discharge processes, which was evaluated from eqns. (3) and (4), is shown in Figs. 2 and 3, respectively. As expected, the concentration of electrolyte decreases when its volume increases. The variations in electrolyte volume and concentration are greatest in the charge, discharge and overdischarge processes. They change to a lesser degree during an open cell overcharge and deep overdischarge while remaining almost unchanged during a closed cell overcharge.
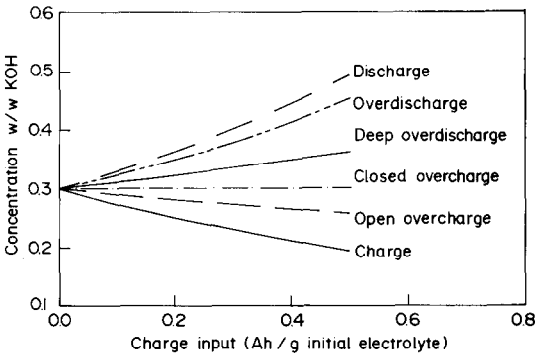

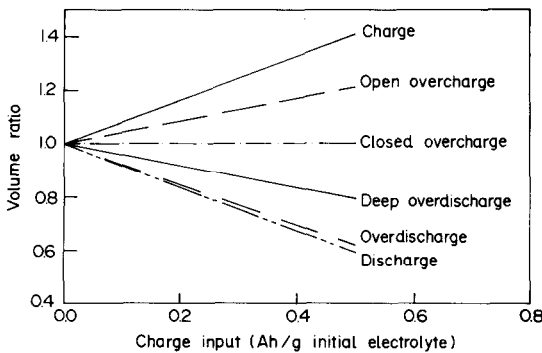Fig. 2. Electrolyte concentration during charge/discharge processes. Initial concentration 0.3 wt./wt. KOH.

Fig. 3. Electrolyte volume variations during charge/discharge processes. Initial concentration 0.3 wt./wt. KOH.

Electrolyte fill volume

Once the water to KOH balance is determined, the electrolyte fill volume can be evaluated. In the production of nickel–cadmium cells, it is a common practice to assemble the cells with 'discharged' negative and positive electrodes and with the negative electrode having excess capacity as described in the 'Introduction'. The ratio of excess negative to positive capacity, R_c, is generally between 0.2 and 0.4 depending on the operating conditions. It is larger for low temperature and high current operation [4]. This uneven capacity causes the cell to be limited by the smaller capacity of the positive electrode which is consumed before the negative one.

Excess of electrolyte restricts oxygen transfer and may cause high pressure buildup. The maximum electrolyte volume in the charged state can be calculated from:

$$V_c = R_e V_{fc} \tag{7}$$

so that

$$V_{fc} = V_{pc} + V_{nc} + V_s \tag{8}$$

where V_s, V_{nc} and V_{pc} are the free volumes in a charged cell of the separator, negative and positive electrodes, respectively and R_e is the desired electrolyte fill ratio which is approximately 0.95 for room temperature operation [5].

Once the charged electrolyte volume V_c and the electrolyte concentration and density in the discharged state (W, D) are known, the required electrolyte fill volume can be calculated.

Equations (1), (2) and (6) are now solved for the electrolyte concentration in the charged cell (W_c), the electrolyte volume in the discharged state (V), and the electrolyte density in a charged state (D_c). First, V and D_c are eliminated, which results in a quadratic equation:

$$(W - W_c)^2 - (W - W_c)D/b + A(D/b)^2/4 = 0 \tag{9}$$

where

$$A = 4b(\Sigma((H_i + K_i)W - K_i)C_i)/(D^2 V_c) \tag{10}$$

The summation in eqn. (10) is carried out for two subsequent processes. First, charging both electrodes to the limit of the positive active material capacity, followed by continued charging until excess oxygen, which did not recombine on the negative electrode, is vented. In this way the negative electrode acquires excess charge until the desired R_c ratio is achieved. These two processes are indicated by reactions 1 (charge) and 3 (overcharge open cell), in Table 1, thus:

$$C_1 = C_p \tag{11}$$

and

$$C_3 = R_c C_p \tag{12}$$

The fact that $W = W_c$ for a process which does not involve any charging ($C_i = 0$) eliminates one of the roots of eqn. (9) leaving only one solution:

$$W_c = W - (1 - (1 - A)^{1/2})D/(2b) \tag{13}$$

W_c from eqn. (13) is now substituted in eqn. (6) in order to evaluate the electrolyte density in the charged state (D_c). V, the electrolyte fill volume in the discharged cell, is then computed from eqn. (4) by substituting D_c:

$$V = (V_c D_c - \Sigma(H_i + K_i)C_i)/D \tag{14}$$

As in eqn. (10), the summation in eqn. (14) is for charge ($i = 1$) and open cell overcharge ($i = 3$).

Figure 4 exhibits the electrolyte concentration in a charged cell and the relative fill volume (V/V_{fc}) *versus* specific loaded capacity (C_p/V_{fc}), for $W = 0.32$, $R_c = 0.3$ and $R_e = 0.95$. The slope in Fig. 4 indicates that the fill volume decreases by a ratio of approximately 0.6 cm^3/A h of the loaded capacity. It is shown below that this decrease greatly affects the cell capacity.
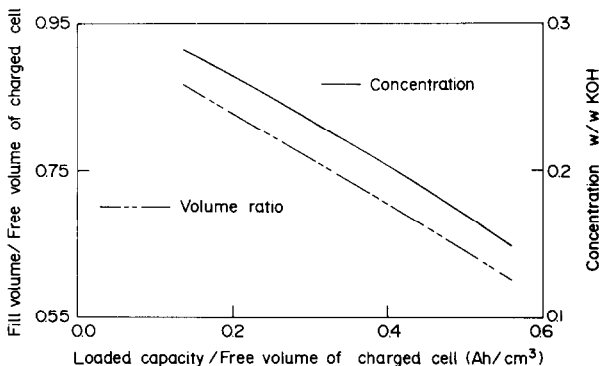

Fig. 4. Electrolyte fill volume and charged concentration *vs.* specific loading.

Electrolyte-limited cell capacity

In the preceding section, the required electrolyte quantity was calculated to ensure that the cell is not flooded in the charged state. This quantity of electrolyte may be too small for the cell during discharge and can limit the capacity. The limit is created by an increase in the cell resistance when the electrolyte occupies less than 70% of the free volume of the separator. This is the reason for using the fraction R_s ($\simeq 0.9$) of the total free volume. The process of electrolyte depletion, outlined in Fig. 3, is partially alleviated during discharge by a decrease of the available free volume. This decreased free volume in the electrodes is due to a volume increase in the active materials during discharge. The result is that, for most of the discharge, the pores are filled with sufficient electrolyte for reasonable electrical conductivity. The increased volume of active materials, cadmium electrode

TABLE 2

Properties of active materials

Formula	Molecular weight (g/mol)	Density (g/cm^3)
Cd(OH)$_2$	146.4	4.79
Cd	112.4	8.64
β_d-Ni(OH)$_2\cdot$0.25H$_2$O	97.2	3.65
β_c-NiOOH$\cdot$0.19H$_2$O$\cdot$0.046KOH	97.7	4.83

and β phase positive electrode during discharge, is demonstrated by the lower densities of the discharged materials, as shown in Table 2 [9 - 11]. With the exception of the β phase of the positive active material, all other phases present in the charged positive electrode are unstable, and decompose to β phase in a matter of a few hours [12] and are therefore not included in the evaluations. The volume change of active material per A h will be:

$$V_{ej} = (M_{dj}/D_{dj} - M_{cj}/D_{cj})/F \tag{15}$$

The minimum volume of electrolyte required to ensure proper electrical conductivity is therefore given by:

$$V_1 = R_s(V_{fc} - C_i\Sigma V_{ej}) \quad j = p, n \tag{16}$$

This minimum free volume, as well as electrolyte volume change, has been evaluated from eqns. (3), (4), (6) and (16) for various values of the specific capacity (C_i/V_{fc}). The results are shown in Fig. 5. It is apparent that the electrolyte volume during discharge may be reduced below the minimum required level such that the cell capacity is restricted. The electrolyte limited capacity can be calculated from these equations by eliminating the discharge variables D, V and W. The solution was obtained by a successive approxima-
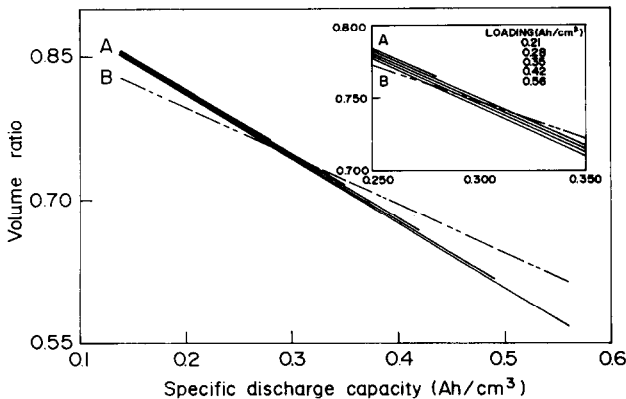

Fig. 5. Electrolyte volume *vs.* discharge capacity per unit free volume in charged cell: (A) electrolyte volume for various active material loading, (B) limiting conditions.
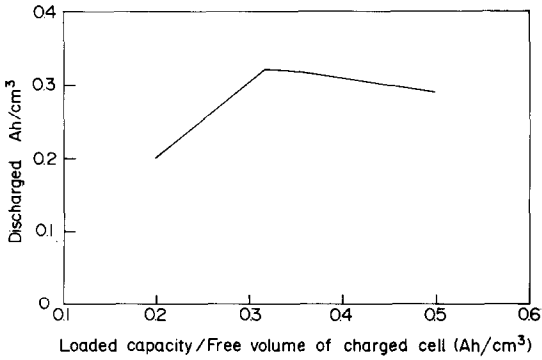
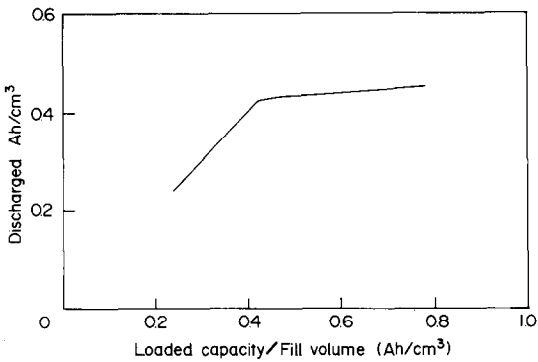Fig. 6. Electrolyte limiting capacity *vs.* specific loading.

Fig. 7. Electrolyte limiting capacity *vs.* specific loading.

tions method via the MINPACK algorithm [13]. The results shown in Figs. 6 and 7, indicate that maximum cell capacity is achieved at about 0.32 A h/cm^3 free charged volume. Above this point the capacity is proportional to the available electrolyte fill volume, as shown in Fig. 7, while below it the capacity increases with active material loading. This ratio of 0.32 A h/cm^3 agrees well with common practice in industry where a rule of thumb calls for 3 cm^3 of electrolyte for each A h capacity of the cell [4].

Conclusions

In sealed nickel–cadmium cells the volume of electrolyte critically influences cell performance. Experimental data obtained in Tadiran (batteries Division) indicated that for a D size, sintered plate cell, a fill volume of 12.6 cm^3 may cause oxygen venting on overcharge. This venting is caused by excessive pressure due to high resistance to oxygen diffusion through the electrolyte. On the other hand a fill volume of less than 11.9 cm^3 in the same cells causes capacity reduction due to insufficient electrolyte on discharge.

This decrease is also accompanied by high electrical resistance and a drop in the cell voltage. The small difference of 0.7 cm³ between the state of excessive electrolyte and starved cell indicates quite clearly that the crude practice of estimating electrolyte fill as a constant fraction of the weight of the core, is unacceptable.

The starved electrolyte condition results in inferior cell life and an unpredictable discharge voltage [14]. On the other hand, increased separator wetting will distribute more electrolyte in it, prevent it from drying out and increase the cell capacity by increasing R_s. Effective electrolyte fill may also be achieved by stabilizing other (than β) positive material phases which have lower densities [10], thus increasing the electrolyte limited cell capacity. Such stabilization may be achieved by active material produced by electrochemical impregnation.

Discharge current level may also affect the capacity of nickel–cadmium cells. At medium and high discharge currents, concentration polarization is produced. The electrolyte hydroxide concentration decreases near the negative electrode reducing the electrolyte conductivity which again reduces the cell capacity. To compensate for this phenomenon the free volume of the discharged negative electrode must be at least 40% of the sintered free volume to provide sufficient supply of hydroxide ions [5]. Similar effects of concentration polarization are treated in ref. 15 for lead–acid cells.

Nomenclature

A	Temporary abbreviation for long expression
b	Slope of density *vs.* concentration correlation (g/cm³)
C_i	Charge quantity (capacity) transferred in process (A h)
C_p	Capacity of positive electrode (A h)
D	Electrolyte density in a discharged cell (g/cm³)
D_c	Electrolyte density in a charged cell (g/cm³)
D_{cj}	Density of charged active material (g/cm³)
D_{dj}	Density of discharged active material (g/cm³)
H_i	Water release coefficient (g/A h)
i	Index to reaction type in Table 1
j	Index to positive or negative electrode
K_i	Base (KOH) release coefficient (g/A h)
M_{cj}	Equivalent weight of charged active material (g/eq.)
M_{dj}	Equivalent weight of discharged active material (g/eq.)
R_c	Ratio of excess charged negative to positive capacity
R_e	Ratio of filled electrolyte to free volume in charged cell
R_s	Ratio of limiting electrolyte to free volume in discharged cell
V	Electrolyte volume in a discharged cell (cm³)
V_c	Electrolyte volume in a charged cell (cm³)
V_{ej}	Specific volume change of active material (cm³/A h)
V_{fc}	Free volume in a charged cell (cm³)

V_1 Limiting electrolyte volume (cm^3)
V_{nc} Free volume in charged negative electrode (cm^3)
V_{pc} Free volume in charged positive electrode (cm^3)
V_s Free volume in separator (cm^3)
W Electrolyte base concentration wt./wt. in discharged cell
W_c Electrolyte base concentration wt./wt. in charged cell
x Water release in reaction per unit charge (mol/eq.)
y Base (KOH) release in reaction per unit charge (mol/eq.)
β_c Phase of positive charged material
β_d Phase of positive discharged material

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Appendix: Calculation of water and base changes

The various reactions mentioned in this work for charge and discharge processes in nickel–cadmium cells are detailed below. Numbers in the heading of each paragraph which describe a set of reactions, correspond to those in Table 1.

Basic KOH–water release coefficients

Variations in quantities of water and KOH during charge are given by:

$$H_i = 18 \text{ (g/mol)} x/26.8 \text{ (A h/eq.)} = 0.6716x \text{ (g } H_2O/A \text{ h)} \qquad \text{(A-1)}$$

$$K_i = 57 \text{ (g/mol)} y/26.8 \text{ (A h/eq.)} = 2.127y \text{ (g KOH/A h)} \qquad \text{(A-2)}$$

where x, y are the molar water and base changes per unit charge and are listed below for the particular reaction.

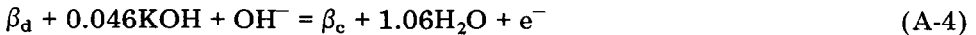Numerical values of these coefficients evaluated from eqns. (A-1) and (A-2) are given in Table 1.

Charge and discharge of active material (i = 1, 2)

The following reactions occur during charge of active materials:
charging of negative active material:

$$Cd(OH)_2 + 2e^- = Cd + 2OH^- \qquad \text{(A-3)}$$

charging of positive active material:

$$\beta_d + 0.046KOH + OH^- = \beta_c + 1.06H_2O + e^- \qquad \text{(A-4)}$$

where

$$\beta_d = Ni(OH)_2 \cdot 0.25H_2O \text{ and } \beta_c = NiOOH \cdot 0.19H_2O \cdot 0.046KOH$$

$$x = 1.06 \qquad y = -0.046$$

During discharge, the signs of x and y as well as the direction of these reactions is reversed.

Charge and oxygen emission in an open cell (i = 3)

During overcharge of a nickel–cadmium cell, oxygen is evolved at the positive electrode. In the formation process of the cell, the negative electrode material is charged. The reactions taking place are:

at the positive electrode: $4OH^- = O_2 + 2H_2O + 4e^-$ $\qquad \text{(A-5)}$

at the negative electrode: $2Cd(OH)_2 + 4e^- = 2Cd + 4OH^-$ $\qquad \text{(A-6)}$
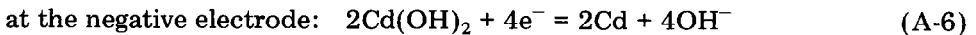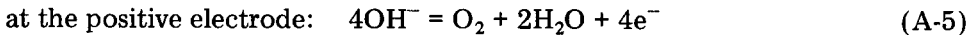
The changes in the water and KOH quantities are therefore:

$$x = 0.5 \qquad y = 0$$

Overcharge of a closed cell (i = 4)

Overcharge occurs when the positive electrode is fully charged while charging current is still supplied. In overcharge of a closed cell, the positive electrode evolves oxygen (eqn. (A-5)) and reacts by recombination with the negatively charged material described by:

$$2Cd + O_2 + 2H_2O = 2Cd(OH)_2 \qquad \text{(A-7)}$$
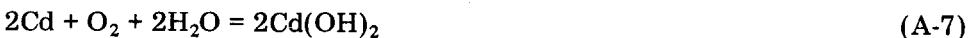
The water which is generated at the positive electrode is consumed by the negative electrode. Therefore no change in the water and KOH quantities occurs.

$$x = y = 0$$

Overdischarge of a closed cell

During overdischarge of a closed cell, hydrogen is evolved from the positive electrode. The hydrogen pressure created in the cell opens the safety valve and releases the excess pressure. The negative electrode, which possesses higher capacity relative to the positive electrode, undergoes discharging for as long as the excess capacity is available. When this normal overdischarge terminates, oxygen is evolved causing excess pressure in the cell.

Two types of overdischarge are therefore identified: normal overdischarge and deep overdischarge.

Normal overdischarge (i = 5)

Hydrogen is evolved by the positive electrode in the reaction:

$$4e^- + 4H_2O = 2H_2 + 4OH^- \tag{A-8}$$

At the negative electrode, the material is discharged following the reversed reaction (A-6). The overall reaction is:

$$2Cd + 4H_2O = 2H_2 + 2Cd(OH)_2 \tag{A-9}$$
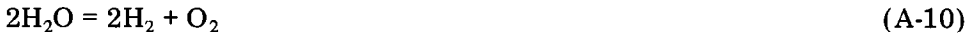
Therefore no change occurs in the KOH quantity in the electrolyte. Water is consumed such that:

$x = -1$ and $y = 0$.

Deep overdischarge (i = 6)

Hydrogen is evolved at the positive electrode following reaction (A-8). At the same time oxygen is evolved at the negative electrode by reaction (A-5), such that the overall reaction is:

$$2H_2O = 2H_2 + O_2 \tag{A-10}$$

Water is therefore dissociated into hydrogen and oxygen such that:

$x = -0.5 \quad y = 0$