

## SPECIFICATION

## Method of precharging the negative electrode of a nickel-cadmium alkaline storage cell

- 5 This invention relates to a method of precharging the negative electrodes of nickel-cadmium alkaline storage cells, and is particularly useful in precharging the negative electrodes of sealed, semi-sealed or semi-open cells. 5

Precharging of the negative electrode of a nickel-cadmium alkaline storage cell consists in establishing a state of charge such that the charged capacity of the negative electrode after precharging is greater than the charged capacity of the positive electrode. To avoid the evolution of hydrogen in sealed cells, it is known to provide the negative electrode with greater charge capacity than the positive electrode, so that, when the positive electrode reaches its fully charged state, the negative electrode still possesses some uncharged capacity. If the negative electrode is precharged by an amount which is less than the difference between the negative and positive electrode charge capacities before the positive electrode is charged, the negative electrode will still possess some uncharged capacity on completion of charging of the positive electrode. Furthermore, after the positive electrode has been fully discharged, the negative electrode will still be partly charged. As a result, the end of discharge is clearer, and the capacity of cells with precharged negative electrodes is more stable during cycling. 10 15

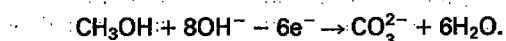
It would appear fairly simple to impart this state of charge by charging the cell while in the open state beyond the point at which the positive electrode is fully charged and up to the level at which the negative electrode possesses the required excess charge, but, in cells with thin electrodes which are close together, it is known that, once the positive electrode has been fully charged, the charge efficiency of the negative electrode becomes very low or even zero. The quantity of charge effectively stored on the negative electrode does not therefore correspond to the quantity of electricity supplied at this point. On the other hand, if it is sought to impart the required charge to the negative electrode before assembling the cell, it is found that the charge does not remain stable during handling of the negative electrode, due to the reactivity of reduced cadmium. 20 25

It is known from British Patent Specification No. 1,362, 039 to fix the relative states of charge of the electrodes of an alkaline storage cell, in which the negative electrode has a charge capacity greater than that of the positive electrode, by charging the cell in the open state and by imparting a sufficient overcharge to it, after fully charging the positive electrode, for the negative electrode to be in a state of charge such that its charged capacity is greater than that of the positive electrode. Since the excess charged capacity must be accurately determined, the overcharge is carried out at a temperature of about  $-10^{\circ}\text{C}$ . Preferably, the excess charged capacity of the negative electrode lies between 10 and 50% of the difference between the real overall charge capacity of the negative electrode and the charge capacity of the positive electrode. Such a method is difficult to carry out, however, since it is necessary to operate at a low temperature. 30 35

Furthermore, in some cases in which the required precharge is to be made on the positive electrode, it has been proposed to introduce into the cell a chemical oxidizing agent which transforms nickel hydroxide into higher hydroxides to apply the precharge. However, transposition of this method to precharging the negative electrode by means of cadmium hydroxide reducers has hitherto not been possible, as cadmium hydroxide is chemically much too stable. 40

According to the present invention there is provided a method of precharging the negative electrode of a nickel-cadmium alkaline storage cell having electrodes assembled in an at least partially discharged state, wherein before the first charge of the cell, a calculated quantity of a material is introduced into the cell, said material being methanol, ethanol or propanol and being able to be irreversibly anodically oxidised substantially without evolving any gas before any nickel hydroxide is oxidised, and then the storage cell is charged in the normal way. 45

In the present invention the substance added, namely methanol, ethanol or propanol, is irreversibly oxidized electrochemically in an alkaline medium without evolving gas to any substantial extent, by producing water and carbonate ions, as in the following reaction exemplified by methanol:- 50

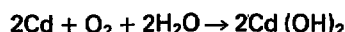


Because it is desirable to keep the formation of carbonate ions to a low value, and because, at the same time, in order to provide a large quantity of electricity, it is advantageous to have the coefficient of  $\text{e}^-$  in the above equation as large as possible, the three alcohols, methanol, ethanol and propanol, are the compounds from which the selection of added substance is made. 55

Each added substance will produce, at least theoretically, an equal quantity of carbonate ions for the same quantity of electricity. The only considerations which then affect the choice of chemical reducing substance are considerations of solubility, ease of electrochemical oxidation, and cost. In the class of substances having the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ , problems of solubility commence at  $n = 4$  (i.e., butanol); for this reason, the above-mentioned three alcohols are used as the substance to be used in precharging the negative cadmium electrode of a nickel-cadmium cell in accordance with the present invention. 60

Utilizing this precharging method, cadmium is formed only during the first charge after the cell has been closed; this has the advantage of avoiding precharge before assembly and the consequent discharge 65

reaction of cadmium in contact with the oxygen in the air according to the following reaction:

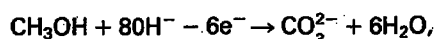


- 5 Furthermore the precharge rate can be accurately determined by appropriately choosing the quantity of the substance added to the electrolyte. 5

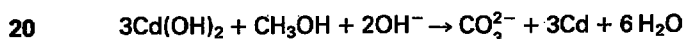
In order that the present invention may be more fully understood, a preferred embodiment of the method of the present invention will now be described by way of example.

#### 10 Example 10

In this example, methanol, which is capable of being oxidized in an alkaline medium according to the following reaction:



- 15 was used as the chemical substance added, the capacity required for this oxidation being 5Ah/g of methanol. 15  
The methanol was then placed in a nickel-cadmium storage cell, the overall charging reaction of the storage cell while the methanol was being oxidized being:



The metal cadmium thus formed represented the precharged capacity.

After the methanol had been used up, the conventional charging reaction of the storage cell took place normally.

- 25 Several series of sealed nickel-cadmium storage cells were assembled, each of which had a nominal capacity of 0.5 Ah. The various series of cells were as follows: 25

Standard: cells whose negative electrodes have received no precharge.

- 30 Series 1: cells whose negative electrodes have been electrochemically precharged at 100 mAh before the electrodes were assembled. 30

Series 2: cells similar to Series 1, but the precharge was at 200 mAh.

- 35 Series 3: cells similar to Series 1, but the precharge was at 300 mAh. 35

Series M<sub>1</sub>: cells whose negative electrodes have received no electrochemical precharge before assembly, but in which 20 mg of methanol have been added to the electrolyte, corresponding to a precharge of 100 mAh.

- 40 Series M<sub>2</sub>: cells similar to Series M<sub>1</sub>, but in which 40 mg of methanol have been added to the electrolyte, corresponding to a precharge of 200 mAh. 40

- 45 Series M<sub>3</sub>: cells similar to Series M<sub>1</sub>, but in which 60 mg of methanol have been added to the electrolyte, corresponding to a precharge of 400 mAh. 45

These cells were subjected to charging cycles each consisting of a charge of 50 mA for 14 hours followed immediately by a discharge at 1A down to a terminal voltage of 0.9V. The results obtained are set out in the tables at the end of the description, in which:

- 50 Table I illustrates the capacities of the various cells after 3, 4, 6, 9, 15, 36, 62 and 138 cycles respectively. 50

Table II shows the efficiency E of the precharge as a percentage, this efficiency being defined by the difference between the capacity of the precharged cell and the capacity of the non-precharged cell divided by the precharge introduced.

- 55 Table I shows that in general a precharge either by the electrochemical method or in accordance with the present invention appreciably increases the cycling capacity. Indeed, from the 3rd cycle onwards, the standard storage cell has a capacity of only 322 mAh instead of the nominal capacity of 500 mAh. In contrast, the capacities of the storage cells of Series 1, 2 and 3 lie between 377 and 454 mAh and those of the storage cells of Series M<sub>1</sub>, M<sub>2</sub> and M<sub>3</sub> lie between 407 and 451 mAh. At the 138th cycle these capacities are respectively: 280 mAh for the standard storage cell, between 284 and 360 mAh for the storage cells of Series 1, 2 and 3, and between 314 and 410 mAh for the storage cells of Series M<sub>1</sub>, M<sub>2</sub> and M<sub>3</sub>. It will be observed that the higher the precharge, the greater the remaining capacity. Such a result agrees, moreover, with the well known fact that, during slow charge-rapid discharge type cycles, a disadvantageous increase in the cadmium grain size is observed, such grains losing their ability to discharge. 60

The precharge therefore provides a reserve of dischargeable cadmium.

- 65 Table II shows firstly that the efficiency of the electrochemical precharge is generally less than that of the 65

methanol precharge and secondly that, although it has a tendency to decrease during cycling, the efficiency of the methanol precharge remains much more constant, at about 50%.

The use of methanol as the precharging substance has been described hereinabove. It will be appreciated that substitution of reduced molar quantities (by a factor equal to the reciprocal of x) of ethanol or propanol for the methanol will yield comparable results because of the above-mentioned characteristic that each will produce an equal quantity of carbonate ions and electricity per atom of carbon.

The method in accordance with the present invention therefore makes it possible to impart to the negative electrode of an alkaline storage cell, of the nickel-cadmium type, a precharge which is strictly predetermined, after crimping or closing said storage cell, thus avoiding the disadvantages due to electrochemical precharging methods.

| Cycle No. | Standard S | Electrochemical precharge |     |     | Methanol precharge |                |                |
|-----------|------------|---------------------------|-----|-----|--------------------|----------------|----------------|
|           |            | 1                         | 2   | 3   | M <sub>1</sub>     | M <sub>2</sub> | M <sub>3</sub> |
| 15        |            |                           |     |     |                    |                |                |
|           | 3          | 322                       | 377 | 432 | 407                | 415            | 451            |
|           | 4          | 304                       | 348 | 428 | 389                | 430            | 450            |
|           | 6          | 292                       | 327 | 395 | 357                | 405            | 428            |
| 20        | 9          | 305                       | 331 | 401 | 363                | 409            | 430            |
|           | 15         | 304                       | 324 | 404 | 360                | 416            | 451            |
|           | 36         | 309                       | 329 | 394 | 362                | 415            | 453            |
|           | 62         | 292                       | 302 | 371 | 343                | 410            | 446            |
| 25        | 138        | 280                       | 284 | 325 | 314                | 376            | 410            |

Table I — Capacities (mAh) of cells after 3, 4, 6, 9, 15, 36, 62 and 138 cycles in which discharge is stopped at 0.9V after a 14 hour charge at C/10, no rest, and a discharge at 2C, where C is the nominal capacity.

| 30        |     | Electrochemical precharge |    |    | Methanol precharge |                |                | 30 |
|-----------|-----|---------------------------|----|----|--------------------|----------------|----------------|----|
| Cycle No. |     | 1                         | 1  | 3  | M <sub>1</sub>     | M <sub>2</sub> | M <sub>3</sub> |    |
| 35        | 3   | 55                        | 55 | 44 | 85                 | 46             | 43             | 35 |
|           | 4   | 44                        | 62 | 47 | 85                 | 63             | 49             |    |
|           | 6   | 35                        | 51 | 41 | 65                 | 56             | 45             |    |
|           | 9   | 26                        | 48 | 43 | 58                 | 52             | 42             |    |
| 40        | 15  | 20                        | 50 | 41 | 56                 | 56             | 49             | 40 |
|           | 36  | 20                        | 47 | 37 | 51                 | 53             | 48             |    |
|           | 62  | 10                        | 40 | 36 | 51                 | 59             | 51             |    |
|           | 138 | 4                         | 22 | 27 | 34                 | 43             | 43             |    |

Table II — Efficiency of the precharge (%)  
(Capacity of a non-precharged storage cell — capacity of a precharged storage cell) / precharge introduced.

## CLAIMS

1. A method of precharging the negative electrode of a nickel-cadmium alkaline storage cell having electrodes assembled in an at least partially discharged state, wherein, before the first charge of the cell, a calculated quantity of a material is introduced into the cell, said material being methanol, ethanol or propanol and being able to be irreversibly anodically oxidised substantially without evolving any gas before any nickel hydroxide is oxidised, and then the storage cell is charged in the normal way.

2. A method according to claim 1 of precharging the negative electrode of a nickel-cadmium alkaline storage cell, which method is substantially as hereinbefore described with reference to the foregoing example.

3. A nickel-cadmium alkaline storage cell whose negative electrode has been precharged by a method according to either preceding claim.



methanol precharge and secondly that, although it has a tendency to decrease during cycling, the efficiency of the methanol precharge remains much more constant, at about 50%.

The use of methanol as the precharging substance has been described hereinabove. It will be appreciated that substitution of reduced molar quantities (by a factor equal to the reciprocal of  $x$ ) of ethanol or propanol for the methanol will yield comparable results because of the above-mentioned characteristic that each will produce an equal quantity of carbonate ions and electricity per atom of carbon.

The method in accordance with the present invention therefore makes it possible to impart to the negative electrode of an alkaline storage cell, of the nickel-cadmium type, a precharge which is strictly predetermined, after crimping or closing said storage cell, thus avoiding the disadvantages due to electrochemical precharging methods.

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|-----------|------------|---------------------------|-----|-----|--------------------|-------|-------|
|           |            | 1                         | 2   | 3   | $M_1$              | $M_2$ | $M_3$ |
| 15        |            |                           |     |     |                    |       |       |
|           | 3          | 322                       | 377 | 432 | 407                | 415   | 451   |
|           | 4          | 304                       | 348 | 428 | 389                | 430   | 450   |
|           | 6          | 292                       | 327 | 395 | 357                | 405   | 428   |
| 20        | 9          | 305                       | 331 | 401 | 363                | 409   | 430   |
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|           | 138        | 280                       | 284 | 325 | 314                | 376   | 410   |
| 25        |            |                           |     |     |                    |       |       |

Table I — Capacities (mAh) of cells after 3, 4, 6, 9, 15, 36, 62 and 138 cycles in which discharge is stopped at 0.9V after a 14 hour charge at C/10, no rest, and a discharge at 2C, where C is the nominal capacity.

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|-----------|-----|---------------------------|----|----|--------------------|----------------|----------------|
|           |     | 1                         | 1  | 3  | M <sub>1</sub>     | M <sub>2</sub> | M <sub>3</sub> |
| 35        | 3   | 55                        | 55 | 44 | 85                 | 46             | 43             |
|           | 4   | 44                        | 62 | 47 | 85                 | 63             | 49             |
|           | 6   | 35                        | 51 | 41 | 65                 | 56             | 45             |
|           | 9   | 26                        | 48 | 43 | 58                 | 52             | 42             |
| 40        | 15  | 20                        | 50 | 41 | 56                 | 56             | 49             |
|           | 36  | 20                        | 47 | 37 | 51                 | 53             | 48             |
|           | 62  | 10                        | 40 | 36 | 51                 | 59             | 51             |
|           | 138 | 4                         | 22 | 27 | 34                 | 43             | 43             |

Table II — Efficiency of the precharge (%)  
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3. A nickel-cadmium alkaline storage cell whose negative electrode has been precharged by a method according to either preceding claim.