

THIS SHEET HAS BEEN
REPLACED

Description

The invention relates to a galvanic cell which comprises an anode gel containing mercury-free zinc powder, and further comprises an alkaline electrolyte and a cathode material which is separated therefrom by a separator and contains manganese dioxide.

Batteries of the abovementioned type are known as alkaline manganese primary cells. Because, on the grounds of protection of the environment, mercury is no longer being added to zinc powder, the anode material of cells of the abovementioned type is subject to increased corrosion which manifests itself in a higher self-discharge and a corresponding gassing rate. Numerous earlier attempts have been made to avoid these negative effects. For example, the zinc used as zinc powder has been alloyed with the metals bismuth, indium, lead, aluminum and calcium (see US-A 5209995). It is also known for the anode gel to be admixed with inorganic gassing inhibitors such as barium hydroxide (see US-A 4418130). EP-A 582293 additionally discloses the addition of an indium salt to the electrolyte.

A further reduction of the gassing rate is desirable on the grounds of costs and with a view to improving the discharge behavior and increasing the capacity of the cells.

It is an object of the invention to provide a solution to the abovementioned problems.

This object is achieved according to the invention in that wherein the cathode material of cells of the abovementioned type contains salt-like calcium compounds in solid form.

Further advantageous refinements of the subject-matter of the invention are disclosed in the subordinate claims.

The effect displayed by the addition, according to the invention, of $\text{Ca}(\text{OH})_2$ and/or CaSO_4 is very largely independent of the grade of zinc used or the alloy components it comprises. Hitherto, when electrolyte-containing cathode materials were used, an increase in

cell gassing has been observed. This effect is due to increased tool wear and a concomitant introduction of heavy metals into the cathode material. By virtue of the addition according to the invention, gassing is brought
5 back to the known level. It was also found that the addition according to the invention reduces gassing in partially discharged cells and improves the discharge capacity of the cells. The capacity which can be drawn from the cells is increased, both for constant discharge
10 and for intermittent discharge.

The invention is explained in more detail with reference to Figures 1 to 6 and to the examples.

Figures 1 and 2 show the discharge curves of Comparative Example 1 and of Example 1 for intermittent
15 discharge of one hour twice a day (2×1 h/d), across a 3.9 ohm resistor of freshly fabricated cells, ie. the storage time N0 indicates cells which have not been stored.

Figures 3 and 4 show the discharge curves of Comparative Example 1 and Example 1 under the same
20 discharge conditions as mentioned above, after the cells had been stored for one month at 70°C (MT 1).

Figures 5 and 6 give the discharge curves of Comparative Example 3 and Example 3, which were obtained
25 for constant discharge across a 2 Ω resistor. The cells were stored for 7 days at 70°C (7MT).

Example 1:

40 experimental cells of size LR14 are assembled according to the following formulation:

30 Cathode material:

paste comprising 8500 g of MnO_2 , 850 g of graphite, 50 g of Ca(OH)_2 , 600 g of electrolyte (50% strength KOH).

Anode gel:

680.0 g of zinc powder, 5.0 g of thickener (carboxylated
35 cellulose), 0.25 g of indium oxide, 0.04 g of Ca(OH)_2 , 314.71 g of electrolyte.

Electrolyte: 760.0 g of 50% strength KOH, 20.0 g of ZnO ,
220.0 g of H_2O

Separator:

honeycomb separator made of poly(vinyl acetate) batt (PVA batt).

Per cell, 32.7 g of cathode material, 4.0 g of electrolyte for impregnating the separator, and 16 g of anode gel are used. The cell jar used is a steel jar having a 0.2 μm nickel and a 0.2 μm cobalt coating.

Comparative Example 1: similarly to Example 1, experimental cells are made which do not contain any calcium hydroxide in the cathode material.

Tables 1 and 2 show comparison of the discharge characteristics of experimental cells made in accordance with Example 1 and Comparative Example 1, respectively. In each case, the values of cells which have not been stored (storage time N0 = fresh) and after a storage time of 1 month (28 days) at 70°C = MT1 were compared, the experimental cells in Table 1 being subjected to intermittent discharge of 2 x 1 hour a day (2 x 1 h/d) across a resistor R = 6.8 Ω . This discharge mode is a model for discharge conditions in a portable tape recorder.

The discharge of the experimental cells in Table 2 took place under intermittent conditions, 4 minutes' discharge, 15 minutes' pause for 8 hours a day (4'/15' 8 h/d) across a 3.9 Ω resistor. This discharge mode is a model for discharge for lighting purposes.

Example 2:

Experimental cells of size LR20 are assembled according to the following formulation:

cathode material: 8500 g of MnO_2 , 850 g of graphite, 600 g of electrolyte (50% strength KOH)

Anode gel: 680.0 g of zinc powder, 5.0 g of thickener (carboxylated cellulose), 0.25 g of indium oxide, 0.04 g of $\text{Ca}(\text{OH})_2$, 314.71 g of electrolyte (38% strength KOH + 2% of ZnO)

Separator: honeycomb separator made of PVA batt.

Per cell, 69 g of cathode material, 9.0 g of electrolyte for impregnating the separator, and 37.5 g of anode gel are used. The cell jar used is a steel jar having a 0.2 μm nickel and a 0.2 μm cobalt coating.

Comparative Example 2

Similarly to Example 2, experimental cells are made which do not contain any calcium hydroxide in the cathode material.

5 Table 3 shows the discharge characteristics at intermittent discharge, 2 x one hour per day (2 x 1 h/d) across a resistor of 3.9 Ω and 2.2 Ω , respectively, as a model of discharging through a tape recorder, cells which had not been stored (N0) being compared with cells after
10 a storage time of 1 month at 70°C (MT1) and with cells which had been stored for 3 months at 45°C (T3).

Example 3

Experimental cells of size LR14 were assembled according to the following formulation:

15 Cathode material: paste comprising 600 g of electrolyte, 8500 g of MnO_2 and 850 g of graphite, 50 g of calcium hydroxide,

Anode gel: 680 g of zinc powder, 5.0 g of thickener, 0.25 g of indium oxide, 0.13 g of indium sulfate, 3.4 g of
20 water, 0.12 g of calcium hydroxide, 311.10 g of electrolyte.

Electrolyte: 760 g of 50% strength KOH, 40.0 g of ZnO , 200.0 g of water

Separator: honeycomb impregnated with 4.0 g of electrolyte.
25

Per cell, 32.1 g of cathode material and 16 g of anode gel are used.

The cell container used is a steel jar coated with 0.2 μm of nickel and 0.4 μm of cobalt.

30 Table 4 shows the discharge characteristics of the trial cells after storage times of N0, 7MT and MT1 for constant discharge across a 2 ohm resistor.

The advantageous effect of the addition according to the invention can be observed, in particular, with
35 intermittent discharge and, in that case, preferably after storage (7MT, MT1 or T3 storage). The differences in capacities in this situation may be up to 20%.

Table 1

Comparison of discharge characteristics for intermittent discharge

2 x 1 h/d across a 6.8 ohm resistor

0% of Ca(OH)₂ in the cathode

Storage time: N0

End voltages:			0.90 (V)			0.80 (V)		
OCV	CCV*		t(h)	Q(Ah)	A(Wh)	t(h)	Q(Ah)	A(Wh)
1.584	1.409		17.00	4.81	5.36	18.05	5.04	5.55
1.584	1.393		16.08	4.53	5.02	18.06	4.98	5.41
1.586	1.397		17.01	4.77	5.26	18.06	5.00	5.46
1.586	1.387		16.07	4.53	5.03	18.06	4.98	5.42
1.584	1.405		16.07	4.57	5.11	18.04	5.00	5.48
$\bar{X}$	1.585	1.398	16.45	4.64	5.16	18.05	5.00	5.47
S	0.001	0.009	0.51	0.14	0.15	0.01	0.03	0.06

0.5% of Ca(OH)₂ in the cathode

0.90 (V)			0.80 (V)		
t(h)	Q(Ah)	A(Wh)	t(h)	Q(Ah)	A(Wh)
16.83	4.78	5.33	19.03	5.25	5.74
16.92	4.75	5.24	19.04	5.21	5.63
16.08	4.57	5.11	18.07	5.01	5.49
16.10	4.54	5.03	18.08	4.97	5.40
16.28	4.64	5.20	19.03	5.24	5.71
16.44	4.65	5.18	18.65	5.14	5.60
0.40	0.11	0.12	0.53	0.13	0.14

Storage time: MT1

End voltages:			0.90 (V)			0.80 (V)		
OCV	CCV*		t(h)	Q(Ah)	A(Wh)	t(h)	Q(Ah)	A(Wh)
1.556	1.423		12.06	3.55	4.12	14.06	3.99	4.50
1.558	1.411		12.04	3.54	4.10	14.07	3.99	4.49
1.558	1.425		13.04	3.79	4.34	15.05	4.23	4.72
1.556	1.417		13.01	3.79	4.35	15.04	4.23	4.73
1.556	1.415		13.04	3.81	4.38	15.05	4.25	4.76
$\bar{X}$	1.557	1.418	12.64	3.70	4.26	14.65	4.14	4.64
S	0.001	0.006	0.53	0.54	0.14	0.14	0.54	0.13

0.90 (V)			0.80 (V)		
t(h)	Q(Ah)	A(Wh)	t(h)	Q(Ah)	A(Wh)
15.90	4.62	5.29	17.50	4.97	5.58
15.79	4.60	5.28	18.16	5.12	5.72
15.56	4.52	5.16	17.45	4.93	5.52
15.46	4.46	5.08	17.42	4.90	5.45
15.49	4.50	5.16	17.36	4.91	5.51
15.64	4.54	5.19	17.58	4.97	5.56
0.19	0.07	0.09	0.33	0.09	0.10

Table 2

Comparison of discharge characteristics for intermittent discharge
4'/15' 8 h/d across a 3.9 ohm resistor

0% of Ca(OH)_2 in the cathode
Storage time: N0

End voltages:			0.90 (V)			0.80 (V)		
OCV	CCV*		t (h)	Q (Ah)	A (Wh)	t (h)	Q (Ah)	A (Wh)
1.584	1.405		14.00	4.10	4.71	17.10	4.87	5.45
1.586	1.405		13.53	3.93	4.49	17.09	4.82	5.34
1.584	1.431		13.40	3.94	4.56	17.07	4.84	5.42
1.584	1.435		13.93	4.09	4.73	17.07	4.87	5.47
1.584	1.397		14.17	4.14	4.75	17.07	4.86	5.45
$\bar{X}$	1.584	1.415	13.81	4.04	4.65	17.08	4.85	5.43
S	0.001	0.017	0.33	0.10	0.12	0.02	0.02	0.05

0.5% of Ca(OH)_2 in the cathode

0.90 (V)			0.80 (V)		
t (h)	Q (Ah)	A (Wh)	t (h)	Q (Ah)	A (Wh)
13.47	4.00	4.65	17.07	4.88	5.49
13.53	4.00	4.64	17.08	4.87	5.47
13.43	3.92	4.47	17.09	4.82	5.34
13.80	4.06	4.68	17.10	4.87	5.47
13.47	3.97	4.60	17.09	4.86	5.45
13.54	3.99	4.61	17.09	4.86	5.44
0.15	0.05	0.08	0.01	0.02	0.06

Storage time: MT1

End voltages:			0.90 (V)			0.80 (V)		
OCV	CCV*		t (h)	Q (Ah)	A (Wh)	t (h)	Q (Ah)	A (Wh)
1.558	1.417		9.99	3.07	3.71	12.33	3.64	4.25
1.558	1.419		10.03	3.09	3.73	12.33	3.65	4.26
1.558	1.411		10.55	3.23	3.89	12.33	3.66	4.30
1.558	1.431		10.65	3.25	3.90	12.33	3.66	4.27
1.556	1.431		10.63	3.24	3.89	12.33	3.66	4.27
$\bar{X}$	1.558	1.422	10.37	3.18	3.82	12.33	3.65	4.27
S	0.001	0.009	0.33	0.09	0.10	0.00	0.01	0.02

0.90 (V)			0.80 (V)		
t (h)	Q (Ah)	A (Wh)	t (h)	Q (Ah)	A (Wh)
14.04	4.25	5.05	16.18	4.77	5.55
13.97	4.22	5.01	16.28	4.79	5.56
14.16	4.28	5.08	16.32	4.81	5.59
14.03	4.25	5.06	16.15	4.77	5.55
14.31	4.32	5.11	16.41	4.84	5.61
14.10	4.26	5.06	16.27	4.80	5.57
0.14	0.04	0.04	0.11	0.03	0.03

Table 3

Comparison of discharge characteristics for
intermittent discharge

2 x 1 h/d across a 3.9 ohm resistor

0% of Ca(OH)₂ in the cathode

0.5% of Ca(OH)₂ in the cathode

Storage time: M0

End voltages:		0.90 (V)		
OCV	CCV*	t (h)	Q (Ah)	A (Wh)
1.584	1.342	38.9	11.13	12.57
1.584	1.372	38.9	11.28	12.90
1.584	1.328	38.9	11.21	12.74
1.584	1.370	38.9	11.27	12.86
1.584	1.370	38.9	11.15	12.61
$\bar{X}$	1.584 1.356	38.9	11.21	12.74
S	0.000 0.020	0.0	0.07	0.15

End voltages:		0.90 (V)		
OCV	CCV*	t (h)	Q (Ah)	A (Wh)
1.594	1.435	40.2	11.55	13.06
1.592	1.377	40.1	11.49	12.96
1.594	1.439	40.1	11.42	12.81
1.594	1.405	41.3	11.94	13.61
1.595	1.414	40.5	11.60	13.11
0.001	0.029	0.6	0.23	0.35

Storage time: M11

End voltages:		0.90 (V)		
OCV	CCV*	t (h)	Q (Ah)	A (Wh)
1.558	1.445	24.2	7.36	8.83
1.556	1.449	25.1	7.55	8.99
1.556	1.443	23.0	6.87	8.12
1.554	1.443	24.1	7.24	8.63
1.556	1.443	25.2	7.61	9.10
$\bar{X}$	1.556 1.445	24.3	7.32	8.74
S	0.001 0.003	0.9	0.30	0.39

End voltages:		0.90 (V)		
OCV	CCV*	t (h)	Q (Ah)	A (Wh)
1.560	1.467	35.4	10.49	12.28
1.566	1.463	35.6	10.54	12.33
1.566	1.457	36.4	10.70	12.45
1.568	1.461	36.0	10.65	12.45
1.566	1.451	35.6	10.54	12.35
1.565	1.460	35.8	10.58	12.37
0.003	0.006	0.4	0.09	0.07

and 2.2 ohms

Storage time: T3

End voltages:		0.90 (V)		
OCV	CCV*	t (m)	Q (Ah)	A (Wh)
1.572	1.405	766	6.59	7.59
1.572	1.425	768	6.56	7.49
1.574	1.375	768	6.59	7.57
1.572	1.389	707	6.19	7.27
1.572	1.485	704	6.20	7.30
$\bar{X}$	1.572 1.416	743	6.43	7.44
S	0.001 0.043	34	0.21	0.15

End voltages:		0.90 (V)		
OCV	CCV*	t (m)	Q (Ah)	A (Wh)
1.582	1.475	1065	9.09	10.40
1.580	1.467	1040	8.98	10.37
1.582	1.471	1045	8.95	10.27
1.584	1.477	1128	9.60	10.95
1.582	1.469	1068	9.07	10.32
1.582	1.472	1069	9.14	10.46
0.001	0.004	35	0.27	0.28

Table 4

Comparison of discharge characteristics for
constant discharge across a 2 ohm resistor

0% of Ca(OH)₂ in the cathode

0.5% of Ca(OH)₂ in the cathode

Storage time: M0

End voltages:		0.90 volts (base load)		
OCV	CCV	t(min)	Q(mAh)	A(mWh)
1.616	1.369	443.33	3770.87	3875.12
1.616	1.400	452.86	3892.77	4047.64
1.616	1.345	413.75	3424.92	3421.98
1.616	1.380	436.67	3700.39	3790.16
1.615	1.326	411.25	3399.73	3393.99
$\bar{x}$ 1.616	1.364	431.57	3637.73	3705.78
S 0.000	0.029	18.36	217.16	287.41

End voltages:		0.90 volts (base load)		
OCV	CCV	t(min)	Q(mAh)	A(mWh)
1.606	1.464	412.86	3676.22	3960.85
1.606	1.456	410.71	3648.71	3920.27
1.606	1.443	405.00	3596.06	3860.81
1.606	1.455	412.50	3658.03	3923.31
1.605	1.413	374.00	3287.53	3487.49
1.606	1.446	403.01	3573.31	3830.55
0.000	0.020	16.52	162.51	195.09

Storage time M1

End voltages:		0.90 volts (base load)		
OCV	CCV	t(min)	Q(mAh)	A(mWh)
1.608	1.361	259.29	2283.64	2433.04
1.608	1.360	256.67	2242.46	2371.75
1.608	1.328	226.11	1964.22	2062.86
1.608	1.366	251.67	2197.90	2325.63
1.608	1.390	276.25	2435.61	2603.26
$\bar{x}$ 1.608	1.361	254.00	2224.77	2359.31
S 0.000	0.022	18.12	170.91	196.29

End voltages:		0.90 volts (base load)		
OCV	CCV	t(min)	Q(mAh)	A(mWh)
1.593	1.403	320.33	2865.11	3095.49
1.593	1.410	320.00	2864.67	3097.46
1.593	1.430	314.79	2860.29	3141.83
1.593	1.431	314.40	2860.80	3147.50
1.593	1.413	335.13	3013.38	3275.05
1.593	1.417	320.93	2892.85	3151.46
0.000	0.013	8.41	67.41	73.20

Storage time 7MT

End voltages:		0.90 volts (base load)		
OCV	CCV	t(min)	Q(mAh)	A(mWh)
1.588	1.370	169.44	1498.27	1606.99
1.588	1.370	176.82	1577.87	1707.27
1.588	1.371	166.25	1479.81	1597.73
1.588	1.352	167.86	1467.60	1556.17
1.588	1.369	186.00	1626.17	1725.27
$\bar{x}$ 1.588	1.366	173.27	1529.94	1638.69
S 0.000	0.008	8.18	68.85	73.64

End voltages:		0.90 volts (base load)		
OCV	CCV	t(min)	Q(mAh)	A(mWh)
1.571	1.430	222.13	2064.89	2319.22
1.570	1.431	238.04	2201.73	2461.91
1.571	1.433	217.44	2027.18	2283.30
1.571	1.434	236.44	2184.97	2440.73
1.571	1.422	221.67	2055.32	2302.42
1.571	1.430	227.14	2106.82	2361.51
0.000	0.005	9.41	80.42	83.30



Claims:

1. A galvanic cell which comprises an anode gel containing mercury-free zinc powder, and further comprises an alkaline electrolyte and a cathode material which is separated therefrom by a separator and contains manganese dioxide, wherein the cathode material contains salt-like calcium compounds in solid form.
2. The galvanic cell as claimed in claim 1, wherein the cathode material contains from 0.1 to 5% by weight of calcium sulfate and/or calcium hydroxide.
3. The cell as claimed in claim 1, wherein the cathode material contains from 0.3 to 0.8% by weight of calcium hydroxide.
4. The cell as claimed in one or more of claims 1 to 3, wherein the cathode material contains the salt-like calcium compounds in a particle size of from 0.1 μm to 30 μm .
5. The cell as claimed in one or more of claims 1 to 4, wherein from 0.0010 to 0.5% by weight of calcium hydroxide, based on the zinc fraction, are present in the anode gel.
6. The cell as claimed in one or more of claims 1 to 5, wherein from 50 to 500 ppm of indium oxide and/or indium sulfate are present in the anode gel.