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Process for fabricating a galvanic cell

Description

The invention relates to a process for fabricating a galvanic cell which comprises an anode
5 gel containing zinc powder and further comprises an alkaline electrolyte and a cathode material which is separated therefrom by a separator and contains manganese dioxide.

Particulate manganese dioxide, mixed with
10 powdered carbon and/or graphite and with a polymer binder such as polyethylene powder, is used as a cathode material in commercial alkaline manganese cells. This involves compression-molding of the cathode material to produce an annular or tubular
15 molding which is inserted into an electrode jar serving as a current collector at the same time, and is filled, with the interposition of a separator, with an aqueous alkaline solution as the electrolyte and with an anode gel essentially comprising zinc powder, electrolyte and
20 a thickener. Cells of the above-described type have the drawback that their electrical load rating is strongly dependent on the diaphragm resistance of the cathode. There has been no lack of attempts to reduce the diaphragm resistance of the cathode by the cathode
25 material being admixed with 7 - 10% by weight of electrolyte solution in the form of 35 - 52% strength aqueous KOH (see David Linden, "Handbook of batteries and fuel cells, 2nd ed., McGraw-Hill 1995, Chapter 10.3). This procedure does have the drawback that the
30 service life of the pressing dies is reduced.

It is an object of the invention to provide a process which avoids the drawbacks of the known fabrication processes.

This object is achieved according to the
35 invention in that the cathode material of galvanic cells of the abovementioned type is admixed with alkaline electrolyte in solid form.

The fabrication then comprises the following steps:

a) particulate MnO_2 is mixed with a highly disperse, carbon-containing material, a polymer binder, compacted and granulated,

5 b) this compound is mixed with alkaline electrolyte in solid form and is compression-molded to produce an annular electrode into which

c) separated by a separator, the anode gel is filled,

d) aqueous alkaline electrolyte is added and

10 e) the cell is sealed by a cover which serves as an electrode terminal and has a current collector, the alkaline electrolyte being added in solid form in process step a) and/or b).

Highly disperse, carbon-containing material is
15 to be understood as a carbon powder having a particle size in the range from 0.10 μm to 10 μm .

In a further refinement of the invention, 5 - 10% by weight of alkaline electrolyte are added in solid form.

20 Preferably, 7 - 9% by weight of KOH are added in solid form, this being commercial solid KOH with an H_2O content of about 15% by weight.

The commercial solid KOH, prior to being added to the cathode material, is ground to a particle size
25 of 50 - 200 μm , preferably in a grinding mill to which CO_2 -free dry air is admitted. The fines are preferably added in process step a), and the particle size range fraction of 50 - 200 μm is preferably added in process step b), preference being given to the use of
30 encapsulated equipment provided with an extraction device.

Advantageously, the concentration of the electrolytes in the ready-to-use cell is established by means of the separator being impregnated with water or
35 an aqueous KOH solution, the concentration of the aqueous KOH solution preferably being within the range of a 0.5 to 1 molar solution.

As an alternative to the abovementioned procedure, an impregnating station for the compression-

molded cathode rings is provided. In so doing, the aqueous KOH solution is recirculated, the pH of the solution is monitored and, if required, is corrected. To improve electrolyte uptake, a temperature regulation
5 device can additionally be provided which permits the temperature of the impregnating electrolyte to be regulated in the range of from 20°C to 70°C.

The cells fabricated according to the invention are suitable for applications involving intermittent
10 loads, particularly in flashlight equipment. In addition, the general high-current load rating during continuous operation is improved. As well as the capacity of the cells fabricated according to the invention being increased and their high-current load
15 rating being improved, the service life of the pressing dies is significantly extended, compared with the process employing electrolyte-containing cathode material.

The invention is explained in detail with
20 reference to the following examples.

Comparative Example 1

Into cells of size LR6 (Mignon - AA) a cathode
25 material is inserted which contains, per 1000 g,

861 g	of MnO ₂ ,
89 g	of graphite,
5 g	of polyether and
30 45 g	of 50% by weight KOH.

Example 1

In a manner similar to Comparative Example 1,
35 cells were fabricated which, instead of 6% by weight of a 38% strength aqueous KOH solution, contained 3% by weight of KOH in solid form.

The results of the experiments under the discharge conditions specified are listed in Table 1.

Here, NO refers to the use of freshly fabricated cells which had not been stored, 7MT to the use of experimental cells which had been stored for 7 days at 70°C, and 28MT to the use of experimental cells which had been subjected to storage for 28 days at 70°C.

The cells according to the invention have a reduced internal resistance, a higher voltage level and improved storage behavior.

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Comparative Example 2

Into cells of size LR03 (Mikro - AAA) a cathode material is inserted which contains, per 1000 g,

15

858 g	of MnO ₂ ,
89 g	of graphite,
8 g	of a mixture of polyether and carboxylated cellulose and
45 g	of 38% by weight KOH solution.

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Example 2

In a manner similar to Comparative Example 2, cells were fabricated which, instead of 6% by weight of a 38% strength aqueous KOH solution, contained 3% by weight of KOH in solid form.

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The results of the experiments obtained under the discharge conditions specified are listed in Table 2.

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The cells according to the invention have a reduced internal resistance, a higher voltage level and a higher discharge capacity with intermittent discharge, compared with the comparative cells. Furthermore the cells according to the invention also exhibit a lower gassing rate and thus a lower self-discharge rate.

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Comparative Example 3

In a manner similar to that for Comparative Example 2, cells were fabricated which instead of 6% by weight of a 38% by weight KOH solution contained only 4.5% by weight of the said KOH solution.

Example 3

10 The cells according to the invention were fabricated in a manner similar to that for Comparative Example 3, but instead of the proportion of KOH solution in the cathode material they contained 3% by weight of solid KOH.

15 Table 3 comprises a comparison of the cells according to the invention with the comparative cells under the discharge conditions specified.

Table 1

Discharge behavior of cells of size LR6

Material: Crushing strength:		Comparative Example 1 6%/38% KOH 700 g	Example 1 3% KOH 700 - 800 g	
	Storage	x	x	
U _o (V) s in mV	NO	1.617	1.617	100%
	7MT	1.607	1.605	100%
	28MT	1.587	1.585	100%
U _b (V) s in mV	NO	1.392	1.438	103%
	7MT	1.384	1.435	104%
	28MT	1.327	1.398	105%
3.9 Ohms cont. (0.9V) min.	NO	351	318	91%
	7MT	330	299	91%
	28MT	296	277	94%
3.9 Ohms cont. (0.75V) min.	NO	412	401	97%
	7MT	364	348	96%
	28MT	338	301	89%
1.8 Ohms pulsed flash (1.0V) Cycles	NO	288	267	93%
	28MT	209	267	128%
1.8 Ohms pulsed flash (0.9V) Cycles	NO	584	528	90%
	28MT	377	467	124%
2 Ohms flash (1.0V) Cycles	NO	526	470	89%
	28MT	322	440	137%
2*4h/d-39 Ohms (0.9V) h	NO	77.3	78.5	102%
2*5min./d-39 Ohms (0.8V) min.	NO	410	406	99%
Contact resistance Jar/rings mOhms				
	NO	303	207	68%
Gassing ml	NO	0.3	0.4	
	28MT	0.6	0.9	
Gassing after initial discharge ml	NO	0.7	0.5	
	28MT	1.1	1.3	

Table 2

Discharge behavior of cells of size LR03

Material: Crushing strength:		Comparative Example 2 6%/38% KOH 400 g	Example 2 3% KOH 400 g	
	Storage	x	x	
U _o (V) s in mV	NO	1.615	1.619	100%
	7MT	1.600	1.602	100%
	28MT	1.567	1.572	100%
U _b (V) s in mV	NO	1.280	1.336	104%
	7MT	1.312	1.338	102%
	28MT	1.243	1.301	105%
10 Ohms cont. (0.9V) min.	NO	449	445	99%
	7MT	429	431	100%
	28MT	416	400	96%
3.6 Ohms pulsed flash (1.0V) Cycles	NO	280	290	104%
	28MT	170	221	130%
3.6 Ohms pulsed flash (0.9V) Cycles	NO	550	523	95%
	28MT	340	447	131%
2 Ohms flash (1.0V) Cycles	NO	48	78	163%
	28MT	46	63	137%
2*4h/d-39 Ohms (0.9V) h	NO	64.4	65.5	102%
5.1 Ohms Hift (0.9V) min.	NO	218	211	97%
2*5min./d-39 Ohms (0.8V) min.	NO	161	155	96%
Gassing ml	NO	0.7	0.3	
	28MT	1.5	1.2	
Gassing after initial discharge ml	NO	0.5	0.3	
	28MT	1.0	0.9	

Table 3

Discharge behavior of cells of size LR03

Material: Crushing strength:		Comparative Example 3 4.5%/38% KOH 400 g	Example 3 3% KOH solid 400 g	
	Storage	x	x	
U _o (V) s in mV	N0	1.609	1.610	100.06%
	7MT	1.597	1.601	100.25%
	28MT	1.596	1.577	100.51%
	T1	1.599	1.602	100.19%
	T3	1.573	1.590	101.08%
U _b (V) s in mV	N0	1.356	1.372	101.18%
	7MT	1.333	1.362	102.18%
	28MT	1.303	1.316	101.00%
	T1	1.353	1.375	101.63%
	T3	1.306	1.348	103.22%
10 Ohms cont. (0.9V) h	N0	7.4	7.5	101.35%
	7MT	7.1	7.3	102.82%
	28MT	6.9	7.2	104.35%
3.6 Ohms pulsed flash (1.0V) Cycles	N0	331	320	96.68%
	T3	297	301	101.35%
	28MT	245	257	104.90%
3.6 Ohms pulsed flash (0.9V) Cycles	N0	564	566	100.35%
	T3	521	516	99.04%
	28MT	449	424	94.43
2 Ohms flash (1.0V) Cycles	N0	79	132	167.09
	T3	71	94	132.39
	28MT	69	80	115.94
2*4h/d-39 Ohms (0.9V) h	N0	65.3	61.9	94.79
	T3	62.3	59.5	95.51
2*5min./d-39 Ohms (0.8V) min.	N0	175	177	101.14



1. A process for fabricating a galvanic cell which comprises an anode gel containing zinc powder and
5 further comprises an alkaline electrolyte and a cathode material which is separated therefrom by a separator and contains manganese dioxide, wherein the cathode material is admixed with alkaline electrolyte in solid form.
- 10 2. The process as claimed in claim 1, wherein
 - a) particulate MnO_2 is mixed with a highly disperse, carbon-containing material, a polymer binder, compacted and granulated,
 - b) this compound is admixed with particulate,
15 solid alkaline electrolyte and is compression-molded to produce an annular electrode into which
 - c) separated by a separator, the anode gel is filled,
 - d) aqueous electrolyte is added and
 - 20 e) the cell is sealed by a cover which serves as an electrode terminal and has a current collector, the alkaline electrolyte being added in solid form in process step a) and/or b).
3. The process as claimed in claim 2, wherein 5 -
25 10% by weight of alkaline electrolyte are added in solid form.
4. The process as claimed in claim 3, wherein 7 - 9% by weight of KOH are added in solid form.
5. The process as claimed in either of claims 3 or
30 4, wherein the solid electrolyte added has a particle size of 50 - 200 μm .
6. The process as claimed in one or more of claims 2 to 5, wherein the separator is impregnated with water or an aqueous KOH solution.
- 35 7. The process as claimed in one or more of claims 2 to 6, wherein the cathode rings, prior to insertion into the electrode jar, are impregnated with water or an aqueous KOH solution.

8. The use of a galvanic cell fabricated as claimed in one or more of claims 1 to 7, for use involving intermittent loads through the galvanic cell, particularly in flashlight equipment.

