

SPECIFICATION

Powder-gel anodes and alkaline-MnO₂ cells containing same

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The present invention relates to alkaline cells comprising powder-gel anodes and to alkaline-MnO₂ cells comprising such anodes.

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A conventional type of alkaline cell employs a cathode comprising predominantly an oxidic depolarizer such as manganese dioxide usually admixed with a binder and conductive material such as graphite, steel wool and the like. The anode usually comprises a consumable anodic material such as powder zinc admixed with a gelling agent such as carboxymethyl cellulose, a suitable alkaline electrolyte such as an aqueous potassium hydroxide solution, and, if desired, mercury. The gel anode is then extruded to form a desired shaped electrode. Anode materials and their preparation are described in U.S. Patents 2,938,064 and 2,935,547 issued to K. Kordes and U.S. Patent 2,993,947 issued to E. E. Leger. The above electrodes together with conventional separator material can be assembled into an alkaline-MnO₂/zinc cell.

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Discharging the above described cell on a microampere drain or on very intermittent discharge has resulted in zinc oxide formation in the separator which can result in internal shorts. Specifically, zinc oxide in contact with metallic zinc is known to be conductive and thus an internal electronic path is formed between the anode and cathode. An investigation of the internal shorting problem has revealed the carboxymethyl cellulose to be a major contributor to the transporting and precipitating of the zinc oxide throughout the cell. This internal shorting causes wasteful consumption of the components of the cell resulting in lower output capacity.

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By practice of the present invention there may be provided one or more of the following:-

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(i) an alkaline-MnO₂/zinc cell that can be discharged on microampere drains without internally shorting,

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(ii) an alkaline-MnO₂ cell comprising a powder-gel anode that employs methyl cellulose with carboxymethyl cellulose as the gelling agent,

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(iii) an alkaline cell comprising a powder-gel anode comprising powder zinc, methyl cellulose, carboxymethyl cellulose and an aqueous alkaline electrolyte,

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(iv) the employment of methyl cellulose as a gelling agent and lubricating agent for powder-gel anodes.

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According to the present invention there is provided an alkaline cell, which comprises a cathode, an aqueous alkaline electrolyte solution and a powder-gel anode comprising a major portion of a consumable anodic material such as zinc, a minor amount of methyl cellulose (MOC), a minor amount of carboxymethyl cellulose (CMC) and an aqueous alkaline electrolyte solution such as an aqueous potassium hydroxide solution.

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The powder-gel anode used in the alkaline cell of this invention is ideally suited for alkaline-MnO₂ cells. The amount of methyl cellulose (MOC), com-

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mercially available as Methocel ("Methocel" is a Trade Mark) should preferably range from 1 to 6 per cent based on the total weight of the extruded anode prior to its assembly in a cell. An amount lower than 1 per cent would not provide sufficient binding for the anode while an amount above 6 per cent would replace too much of the active consumable anode material for a given size anode and render the gel too viscous to properly extrude the anode without providing any additional advantage. More preferably the range should be about 2 per cent to about 5 per cent, based on the weight of the extruded anode.

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Methyl cellulose has been found to have no ionic charge and therefore will not form complexes with metallic salts. Contrary to this, carboxymethyl cellulose (CMC), a carboxylic acid, does have an ionic charge and further can be oxidized by the action of manganese dioxide to produce more carboxylic acid groups. It is believed that if a complex between carboxymethyl cellulose and zinc oxide is formed, it also must have an association constant such that a minimum amount of carboxymethyl cellulose and zinc oxide must be in solution so that the product of their concentration exceeds that of the association constant before the solid complex will precipitate. Consequently by reducing the potassium hydroxide concentration, the solubility of zinc oxide is reduced thereby reducing the ionic product to a value close to or below the association constant which can prevent the carboxymethyl cellulose complex from transporting and precipitating the zinc oxide throughout the cell. The same effect is believed true if the carboxymethyl cellulose concentration is reduced. Thus by reducing either the zinc oxide or carboxymethyl cellulose in solution, the complex of these two compounds can be reduced thus resulting in less zinc oxide transported throughout the cell.

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One advantage in the use of carboxymethyl cellulose is that it will cause the anode to swell on contact with the cell electrolyte thereby providing a good anode-to-cathode interface for optimum cell service. In an extruded anode containing methyl cellulose, methyl cellulose was observed to quickly precipitate on contact with the cell electrolyte without allowing the anode to effectively swell. Although the anode can be appropriately formed and positioned to make good contact against the separator/cathode of the cell before the electrolyte is added, it is within the scope of this invention to use a reduced amount of carboxymethyl cellulose along with methyl cellulose in the formation of powder-gel anodes. Thus the advantage of the swelling characteristics obtained through the use of carboxymethyl cellulose can be utilized without the disadvantage of internal shorting since the amount of carboxymethyl cellulose to be used can be greatly reduced from the amount that would normally be employed. For example, normally carboxymethyl cellulose is employed in an amount of about 3.5 to 5 per cent based on the weight of the anode while the amount which can be used along with methyl cellulose in accordance with this invention is only about 0.5 to 2.5 per cent based on the weight of the anode.

Preferably the methyl cellulose can vary from 1 to 4.5 per cent and the carboxymethyl cellulose can

vary from 0.5 to 2.5 per cent based on the weight of the extruded anode. Most preferably, the methyl cellulose should be about 2 per cent and the carboxymethyl cellulose about 1.5 per cent, based on the 5 weight of the anode.

In addition to being a good substitute for carboxymethyl cellulose in powder-gel anodes, methyl cellulose upon precipitating will release or free electrolyte to the cell where it can be used in the electrochemical reaction and/or to improve ionic diffusion in the cell.

The present invention will now be further illustrated by way of the following Examples:

EXAMPLE 1

- 15 Several test lots of alkaline-MnO₂/zinc cells (0.6 ampere-hour capacity) were constructed using electrodes formed from the following mixes: cathode:
- 1.69g manganese dioxide
 - 0.16g graphite
 - 20 0.03g acetylene black
 - 0.23g KOH (37%)

anode:

- 0.74g powdered zinc (about 60 Tyler Mesh size)
- 0.088g 0.1N KOH

25 0.044g mercury

a gelling agent as shown in Table 1.

The above components along with a separator of a fibrous cellulosic material were assembled in a conductive housing and then discharged across various 30 loads, and the times it took to reach various cutoff voltages were observed. The data so obtained are shown in Tables 1 and 2. Cells from the test lots were stored at 54° C or 71° C for various time periods and then the open circuit voltage and current were 35 observed. The data so obtained are shown in Table 3.

As evident from the data shown in the tables, methyl cellulose can effectively be used as a substitute for carboxymethyl cellulose so as to eliminate 40 internal shorting on low drain conditions.

TABLE I

SERVICE (hours)

Resistor	1.0 volt cutoff			0.9 volt cutoff			0.7 volt cutoff		
	Test Lot No.			Test Lot No.			Test Lot No.		
Load (ohms)	1	2	3	1	2	3	1	2	3
12.5 ¹	2.7	2.5	2.4	3.1	3.1	2.6	3.0	3.5	2.7
25 ¹	6.6	6.5	6.8	7.4	7.4	7.8	9.0	9.7	9.6
37.5 ¹	9.4	10.5	10.6	10.2	12.2	12.0	10.5	15.5	14.4
25 ²	6.5	6.5	6.7	7.6	7.8	7.9	8.8	9.5	9.3
83.3 ³	24	25	25	27	29	29	33	36	34
125 ⁴	36	39	38	40	43	42	48	50	50
125 ³	35	37	38	40	43	43	48	52	51
750 ⁴	35	38	38	39	44	43	46	50	50
750 ³	36	38	39	42	44	44	50	52	52

¹-continuous discharge
²-discharge 1/2 hour a day
³-discharge 4 hours a day
⁴-discharge 2 hours a day

Test Lot No. 1=0.032g CMC
2=0.032g MOC
3=0.018g MOC+0.009g CMC

MOC=methyl cellulose, type Methocel A4M Premium
Dow Chemical Co. Midland, Michigan

TABLE II

* SERVICE (Hours)

Voltage Cutoff (volt)	Test Lot 1	Test Lot 2	Test Lot 3
1.3	220	220	220
1.2	320	360	360
1.1	340	440	440
1.0	Shorted	500	500
0.9		600	600
0.8		640	640
0.7		660	660

* Continuous discharge across 1500-ohm load

Test Lot No: 1=0.032g CMC
2=0.032g MOC
3=0.018g MOC+0.009g CMC

TABLE III

	Storage 54°C.						Storage 71°C.					
	Test Lot 1		Test Lot 2		Test Lot 3		Test Lot 1		Test Lot 2		Test Lot 3	
Time	Volts	Amps	Volts	Amps*	Volts	Amps	Volts	Amps	Volts	Amps*	Volts	Amps
Fresh	1.58	4.6	1.60	2.9	1.60	4.4	1.58	4.7	1.61	3.3	1.60	4.0
2 weeks	1.52	4.0	1.57	2.5	1.56	4.0	1.49	3.0	1.54	1.8	1.52	2.9
4 weeks	1.51	3.7	1.56	2.4	1.54	3.7	1.47	2.5	1.52	1.5	1.52	2.3
6 weeks	1.50	3.4	1.55	2.0	1.53	3.2	1.44	2.2	1.51	1.3	1.51	2.1
8 weeks	1.49	3.1	1.54	1.9	1.53	2.9	1.43	1.8	1.50	1.1	1.49	1.7
10 weeks	1.49	2.9	1.54	1.8	1.53	2.7						
12 weeks	1.48	2.9	1.54	1.7	1.53	2.6						

* possibly due to anode not swelling.

Test Lot No. 1=0.032g CMC

2=0.032g MOC

3=0.018g MOC + 0.009g CMC

Volts = open circuit voltage (volts)

Amps = amperes

EXAMPLE 2

Several test lots of cells (0.6 ampere-hour capacity) were produced as shown in Example 1 except that the amounts of methyl cellulose and carboxymethyl cellulose were each varied from 0 to 3.5 per cent based on the weight of the anode while maintaining the total percentage of one or both of these additives at 3.5 per cent based on the weight of the extruded anode. The cells were discharged across a 1500-ohm load and at different ampere-hour intervals a cell from each test lot was disassembled and visually inspected. The data so observed are shown in Table 4.

Again these data demonstrate that methyl cellulose can be substituted for some or all of the carboxymethyl cellulose gelling agent in a powder-gel anode to produce a gel anode that will not internally short under low drain conditions.

TABLE IV

Discharged across a 1500-ohm load

Test Lot No.	* CMC (%)	* MOC (%)	0.172 (Ah) **	0.256 (Ah)	0.335 (Ah)	Internal Shorting
1	3.5	—	ZnO through sep.	ZnO through sep.	ZnO through sep.	Yes at 0.256 Ah
2	3.0	0.5	Lg. amounts of ZnO under sep. little through sep.	Small amount through sep.	"	Yes at 0.256 Ah
3	2.5	1.0	Lg. amount of ZnO under sep. little through sep.	"	"	No
4	2.0	1.5	Moderate amount ZnO under sep. None through sep.	Little amount through sep.	"	"
5	1.5	2.0	Like lot 4 except slightly less ZnO seen	"	Small amount ZnO under sep. None through sep.	"
6	1.0	2.5	Small amount under sep. None through sep.	Like lot 5 except smaller amount through sep.	Very little ZnO through sep.	"
7	0.5	3.0	"	Small amount under sep. None through sep.	Small amount under sep. None through sep.	"
8	—	3.5	Small amount under sep. None through sep.	Very small amount under sep. None through sep.	Small amount under sep. None through sep.	No

1g.=large

sep.=separator

* =based on weight of dry constituents of anode.

** =ampere-hour (Ah)

While the invention has been described in conjunction with specific embodiments, it is obvious that certain modifications may be made to the invention without deviating from the scope of the invention.

CLAIMS

1. An alkaline cell, which comprises a cathode, an aqueous alkaline electrolyte solution and a powder-gel anode comprising a major portion of a consumable anodic material, a minor amount of methyl cellulose, a minor amount of carboxymethyl cellulose and an aqueous alkaline electrolyte solution.

2. An alkaline cell as claimed in claim 1 wherein the electrolyte is an aqueous potassium hydroxide electrolyte.

3. An alkaline cell as claimed in claim 1 or claim 2 wherein the consumable anodic material is zinc powder and the electrolyte solution is aqueous potassium hydroxide.

4. An alkaline cell as claimed in any of claims 1 to 3 wherein the methyl cellulose is present in an

amount of from 1 to 6 per cent, based on the weight of the anode.

5. An alkaline cell as claimed in any of claims 1 to 4 wherein the methyl cellulose is present in an amount of from 1 to 4.5 per cent and the carboxymethyl cellulose from 0.5 to 2.5 per cent, based on the weight of the anode.

6. An alkaline cell as claimed in claim 5 wherein the methyl cellulose is about 2 per cent and the carboxymethyl cellulose is about 1.5 per cent based on the weight of the anode.

7. An alkaline cell as claimed in any of claims 1 to 6 wherein the cathode comprises manganese dioxide.

8. A powder-gel anode as claimed in claim 1 and substantially as hereinbefore described with reference to either of the Examples.

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6	1.0	2.5	Small amount under sep. None through sep.	Like lot 5 except smaller amount through sep.	Very little ZnO through sep.	"
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