THE BENEFICIAL EFFECT OF INCREASED CATHODE WATER CONTENT ON Mg/MnO$_2$ BATTERY PERFORMANCE

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Summary

Characteristically, magnesium/manganese dioxide (Mg/MnO$_2$) batteries perform poorly during periods of intermittent usage. Following removal of the protective magnesium hydroxide film, the anode undergoes corrosion resulting in severe capacity loss of between approximately 21 and 47%. Increasing the cathode water content can enhance battery performance by as much as 31%.
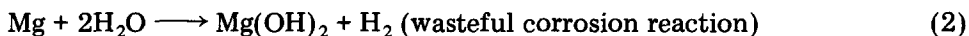
Introduction

Army primary battery systems comprise Leclanché (dry), alkaline, magnesium (Mg/MnO$_2$), and high power lithium/sulfur dioxide (Li/SO$_2$). The most widely used, lithium/sulfur dioxide, vastly outperforms its counterparts. Lithium batteries operate over a wider temperature range (−70 to 160 °F), deliver a higher energy density (300 W h/kg), operate at greater current drains (4 A), and maintain a very flat discharge profile. However, a distinct disadvantage of lithium batteries is their high purchase cost which is 2 - 3 times more than the other primary battery systems. The elevated purchase cost is due mainly to the construction of the pressurized jelly-roll cell design. Presently, the cell manufacturing process is highly labor intensive, thus adding to the greater cost.

A prevalent Army communications equipment, the AN/PRC-77 radio set, is powered by two battery types. One, the magnesium BA-4386/U battery, costs approximately $15. Its counterpart, the lithium BA-5598/U battery costs approximately $35. In the past, the superior lithium battery performance justified the greater cost. However, under certain operating conditions the higher cost may not be warranted. This price differential has resulted in the re-evaluation of magnesium battery usage. A reduction in the negative effects of magnesium battery deficiencies could result in the magnesium battery replacing the lithium system during tepid climate, low drain applications (*i.e.*, classroom training exercises). One major deficiency of the

magnesium system is the magnesium anode corrosion that occurs during storage following partial usage. This corrosion decreases the useful capacity by approximately 30 - 40%.

One characteristic of magnesium/manganese dioxide batteries is the formation of a magnesium hydroxide [Mg(OH)$_2$] film on the magnesium anode. How this film affects the performance of the magnesium batteries is well known [1 - 3]. This oxide film, which results in voltage delay, especially during low temperature operation, also protects the magnesium anode from wasteful corrosion. Once the protective film is removed, by passage of current, the anode is exposed and corrosion occurs. Robinson's [4] explanation for the removal of the film is due to an increased acidity at the anode interface and thus an increased solubility of the magnesium hydroxide film. The film does not fully reform to its original structure, thus the anode efficiency is reduced. This results in capacity loss during storage following partial usage.

For the magnesium system, the two competing reactions are:

$$Mg + 2MnO_2 + H_2O \longrightarrow Mn_2O_3 + Mg(OH)_2 \text{ (current producing reaction)} \quad (1)$$

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2 \text{ (wasteful corrosion reaction)} \quad (2)$$

The corrosion reaction consumes magnesium and water, both necessary for the beneficial current-producing reaction. Various methods of attempting to reduce the negative effects of the magnesium corrosion exist. One method involves the use of a corrosion inhibitor. Presently, the only inhibiting agent used in magnesium batteries is chromate, which is added to both the electrolyte and the cathode mix. A second involves the modification of the cell chemistry so that the protective magnesium hydroxide film easily reforms to its original degree of passivity. Optimization of these measures requires many man-hours of detailed and in-depth research. Naturally, a quick, practical, and simple battery 'fix' is preferred. This paper discusses an effective design modification which is practical and simple enough for quick implementation.

Investigation

The postmortem analysis of several discharged magnesium batteries revealed the presence of large amounts of the magnesium alloy anode (the magnesium can was still intact). The batteries, which were fully discharged, underwent storage following partial usage. The corrosion reaction, upon initiation by the partial discharge scenario, resulted in the increased consumption of both the magnesium anode and the water. Apparently, in the current-producing reaction, the water is the limiting reactant. Sufficient quantities of water are consumed during corrosion to adversely affect battery performance. It was decided to provide greater amounts of water (*i.e.*, increase the initial cathode moisture content).

The viability of beneficially affecting the magnesium battery performance via increasing the cathode moisture content was studied. For the investigation, production BA-4386/U magnesium batteries were tested. The simplicity of the design modification made possible the use of ready-made magnesium batteries.

The BA-4386/U battery consists of 18 long 'C' size cells in series–parallel construction. The battery nominal capacity is 8 A h, with an open circuit voltage of 15 V and an end voltage of 10 V. The cells are of the bobbin construction. The anode, the can itself, is a magnesium alloy (AZ21) that contains small amounts of aluminum, zinc and calcium. The cathode consists of an extruded mix of manganese dioxide (85 - 87%), acetylene black (10%), barium chromate (1 - 3%) and magnesium hydroxide (1%). The electrolyte is an aqueous solution of 4 N magnesium perchlorate [Mg-$(ClO_4)_2$] with lithium chromate added for corrosion inhibition. The separator is an absorbent kraft paper. The cell seal is critical, as it must retain moisture while allowing the escape of hydrogen gas that is produced during the corrosion reaction. The seal is a mechanical vent; a small hole in the top plastic washer that is deformed under pressure, thus releasing the excess gas.

Increasing the cathode moisture content of the magnesium cells involved removing the top of the paper battery casing and exposing the cell tops. Using a 3/32 size drill bit, a hole 1/2 inches deep was drilled into the top of all 18 cells. The bit did not penetrate the cell core; a sufficient void at the cell top made this possible. Following this, 1.0 cc of distilled water was injected into all 18 cells, the holes resealed, and the batteries stored at room temperature for two weeks prior to discharge.

A total of forty-eight BA-4386/U magnesium batteries was tested; twenty-four with no additional moisture and twenty-four with additional water. The discharge load for all the batteries was 130 mA constant current. Prior work [5] involving the testing of magnesium batteries under the AN/PRC-77 radio load scenario (2 min at 14.2 Ω/18 min at 291 Ω) showed that the 130 mA load is comparable, as far as current is concerned, to the AN/PRC-77 radio discharge scenario. The constant current discharge profile was used for ease of performance comparison among the various discharge circuits. The transmit/receive duty cycle regime was not tested.

Three groups of batteries were tested under the following conditions:
- Discharge temperature: 40 and 70 °F
- Additional water added: yes, no
- Intermittent storage temperature: 70 - 75 °F

One group was discharged continuously to an end voltage of 10.0 V. The remaining two groups were initially discharged for two days, 8 h per day, with room temperature storage between each day. Following the initial two-day discharge, the batteries were stored for either one or four weeks at room temperature. The regime, 8 h of 130 mA discharge followed by 16 h of room temperature storage, was then continued until the 10.0 V cutoff was reached.

Results and discussion

The experimental data are presented in Tables 1 and 2, and a summary of the test results is presented in Table 3. The results show that at discharge temperatures of 40 and 70 °F, the additional water enhanced the magnesium battery performance. At 40 °F the capacity, compared to the battery performance with no additional water, increased by 13.3% (continuous discharge), 22.9% (one week intermittent storage) and 28.9% (four weeks intermittent storage).

At 70 °F an improvement in the battery performance under all three storage conditions is also observed. The additional water resulted in an increase in capacity of 2.4% (continuous discharge), 41.2% (one week intermittent storage), and 31.3% (four weeks intermittent storage).

At both discharge temperatures an interesting phenomenon takes place. Table 3 shows that following one week storage, for batteries with additional water, the battery performance is greater than that obtained during con-

TABLE 1

Mg/MnO$_2$ BA-4386/U PRC-77 discharge[a]

Battery number	Water added	Intermittent storage period (weeks)	Service to 10 V (h)
25	yes	0	61.8
26	yes	0	53.3
27	yes	0	62.2
28	yes	0	61.7
29	no	0	55.5
30	no	0	52.9
31	no	0	53.2
32	no	0	50.0
45	yes	1	64.1
46	yes	1	60.5
47	yes	1	62.3
48	yes	1	59.8
37	no	1	52.1
38	no	1	52.2
39	no	1	46.6
40	no	1	49.8
41	yes	4	52.7
42	yes	4	58.9
43	yes	4	59.8
44	yes	4	void
33	no	4	42.7
34	no	4	45.5
35	no	4	45.8
36	no	4	43.2

[a]Discharge rate: 130 mA at 40 °F; intermittent storage temperature: 70 - 75 °F.

TABLE 2

Mg/MnO$_2$ BA-4386/U PRC-77 discharge[a]

Battery number	Water added	Intermittent storage period (weeks)	Service to 10 V (h)
1	yes	0	72.4
2	yes	0	72.6
3	yes	0	68.3
4	yes	0	73.5
5	no	0	66.4
6	no	0	71.4
7	no	0	72.0
8	no	0	67.8
21	yes	1	92.6
22	yes	1	89.8
23	yes	1	88.8
24	yes	1	92.1
13	no	1	44.8
14	no	1	72.5
15	no	1	72.7
16	no	1	67.1
17	yes	4	60.2
18	yes	4	70.8
19	yes	4	79.5
20	yes	4	80.0
9	no	4	void
10	no	4	53.6
11	no	4	51.2
12	no	4	61.2

[a]Discharge rate: 130 mA at 70 °F; intermittent storage temperature: 70 - 75 °F.

tinuous usage. For the batteries with no additional water, the opposite occurs. The performance of the batteries degraded linearly with increased intermittent storage periods. It is theorized that a 'washing' effect, brought on by the additional water, helped to unclog the cathode reaction sites. The cathode efficiency was increased, thus resulting in greater capacity. The benefits of the 'washing' outweigh the detrimental effects of the magnesium corrosion. Following the four week intermittent storage, however, a reduction in the overall positive effect is observed. Any benefits obtained from the 'washing' are negated by the detrimental magnesium corrosion.

Conclusions

From the results described above, the following summarized conclusions have been drawn.

TABLE 3

Mg/MnO$_2$ BA-4386/U PRC-77 discharge testing summary[a]

Water added	Discharge temperature (°F)	Intermittent storage period (weeks)	Service to 10 V		Capacity enhancement (%)
			Mean	Std. dev.	
No	40	0	52.8	1.9	
Yes	40	0	59.8	3.7	13.3
No	40	1	50.2	2.3	
Yes	40	1	61.7	1.7	22.9
No	40	4	44.3	1.4	
Yes	40	4	57.1	3.2	28.9
No	70	0	69.4	2.4	
Yes	70	0	71.1	2.0	2.4
No	70	1	64.3	11.5	
Yes	70	1	90.8	1.6	41.2
No	70	4	55.3	4.1	
Yes	70	4	72.6	8.1	31.3

[a]Discharge rate: 130 mA; intermittent storage temperature: 70 - 75 °F.

(i) The introduction of additional water to the magnesium/manganese dioxide batteries resulted in an enhancement in the capacity during continuous, one week intermittent, and four weeks intermittent discharge.

(ii) The additional water minimized the determinental effect that intermittent usage characteristically has on magnesium/manganese dioxide batteries.

(iii) At 70 °F discharge, the positive effect the additional water has on the magnesium battery capacity is the greatest.

References

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