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Electrochemical Performance of Al/MnO_2 Dry Cells: An Alternative to Lechlanche Dry Cells

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Aluminum-MnO_2 (Al/MnO_2) dry cells of "D" size configuration are investigated as an alternative to the Lechlanche dry cell, where aluminum is replaced for zinc as the anode, MnO_2 as the cathode, and a mixture of aluminum chloride/ammonium chloride/chromium chloride as the electrolyte. Investigations regarding the optimization of conducting material, electrolyte composition, and electrochemical performance of the cell at different temperature and current drains (100, 200, and 400 mA) are carried out. Internal resistance and storage life of the fabricated aluminum dry cells are also evaluated. The results suggest that Al/MnO_2 dry cells exhibit a superior performance than their Zn counterpart.
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Aluminum (Al) is an attractive candidate for use as an anode material in primary batteries,[1] due to its high electrochemical equivalence (2.98 Ah g^{-1}), high standard potential (-1.66 V), and high energy density compared to conventional zinc and magnesium anodes. Its low atomic weight (8.99 g mole^{-1}) and multivalence charge (3 electron transfer) result in a high capacity on both a gravimetric and volumetric basis. Furthermore, Al/MnO_2 dry cells are environmentally benign and much cheaper compared to the commercially available Zn/MnO_2 system available in the market. Al/MnO_2 dry cells have shown almost twice the service life or capacity of a zinc cell of equivalent size and the ability to retain its capacity during storage even at elevated temperatures.[2,3] This excellent storage capability is due to a protective film that forms on the surface of the Al anode used. The common disadvantage with the Al system involves the "voltage delay" and the parasitic corrosion of Al that occurs during the discharge once the protective film is removed, generating H_2 and some heat evolution. This can be tackled by the use of corrosion inhibitors like potassium chromate or dichromate in calculated amounts added to the electrolyte. Due to the high corrosion rate of the Al anode, the shelf life is poor. But, the use of inhibitors which form a protective film over the Al anode when no current is being drawn from the cell could improve the shelf life of the system. The basic anode reaction[4] of aluminum can be represented as

$$Al = Al^{3+} + 3e^- \quad E^0 = -1.6 \text{ V} \qquad [1]$$

The limitations of this anode are high corrosion rate, passivation, and delayed action. Aluminum is used in Al/air reserve batteries employing sodium hydroxide electrolyte. Aluminum chloride is also used as an electrolyte along with a corrosion inhibitor. Corrosion of aluminum is reported to be minimized by alloying with zinc tin, bismuth, and magnesium and by using inhibitors.[4] An acidic electrolyte can be used to break up the film.[5]

A cell with an Al anode should theoretically have a potential of about 0.9 V higher than the corresponding zinc cell, but such a high cell voltage is not achieved with Al systems due to the presence of the protective oxide film on Al. A potential of 0.2 to 0.3 V higher is only achieved for Al/MnO_2 systems compared to zinc systems.[6] In light of the above discussion, we present our investigations on Al/MnO_2 dry cells which have not been extensively studied previously. In the present paper, we report our investigations on the fabrication and electrochemical performance of Al/MnO_2 dry cells at various current drains. A comparison with the conventional Zn/MnO_2 dry cells has also been attempted.

Experimental

Chemicals.— Manganese dioxide (Fluka AG, Switzerland), aluminum chloride, ammonium chloride, chromium chloride (Loba/chemie, AR), acetylene black, and aluminum 2S alloy sheets (commercial), aluminum–magnesium alloy (in-house made) were used. The composition of 2S alloy was Al: 99%; Mg: 0.5%; Fe: 0.4%: Mn: 0.1%, and for aluminum–magnesium alloy (AM alloy) Al: 97.7%; Mg: 2%; Mn:0.3%.

Preparation of Al/MnO_2 dry cell.— A typical cell contains 16 grams of MnO_2, 6.5 grams of acetylene black (AB), 5% binder. Carboxymethyl cellulose was used as a binder, which enables the coherence among the active mass in the form of gel. Cans made out of 2S aluminum sheets/AM alloy were used as the anode. Initially, the electrolyte solution was prepared by dissolving weighed amounts of $AlCl_3$, NH_4Cl, and $CrCl_3$ in distilled water. The contents were then transferred into a bowl containing the cathodic mix (MnO_2 + AB + CMC) and mixed to obtain a wet mass. A calculated quantity of inhibitor was also added. This gel nature of the bobbin mix reduces rather than prevents the easy escape of H_2O during storage and discharge as well. The gelled mixture was transferred into a bobbin-making die set suitable for a "D"-size dry cell. A paraffin-coated carbon rod was inserted in the center and the mix was compacted at a pressure of 200 psi to yield the cathode bobbin. This was then transferred to the can with kraft paper wound over the bobbin.

Optimization of electrolyte.— The electrolyte used for the Al/MnO_2 cells is a mixture of aluminum chloride, ammonium chloride, and chromium chloride. Table I shows the different electrolyte compositions investigated. Al/MnO_2 dry cells were made with varying electrolyte compositions (Table I), fixing the amount of electrolytic manganese dioxide and AB (16 and 6 g, respectively) and were subjected to discharge studies at 100 mA current drain.

Optimization of conducting material.— Natural graphite has been replaced by AB in dry batteries by virtue of its high porous nature, larger surface area for adsorption of electrolyte, and better conductivity. It has been reported that AB in dry cell in the range of 30–35 wt. % of electrolytic manganese dioxide (EMD) showed better performance.[1] MnO_2 is a poor electrical conductor. AB serves the functions of holding the electrolyte mix and providing compress-

Table I. Different electrolyte compositions used for Al/MnO_2 dry cells.

S. No	$AlCl_3$ (g)	NH_4Cl (g)	$CrCl_3$ (g)	AB (g)	MnO_2 (g)
1	2.00	0.5	1.00	6	16
2	2.00	2.00	1.00	6	16
3	2.00	1.5	2.00	6	16
4	1.00	1.5	1.00	6	16
5	2.00	1.5	1.00	6	16
6	3.00	1.5	1.00	6	16

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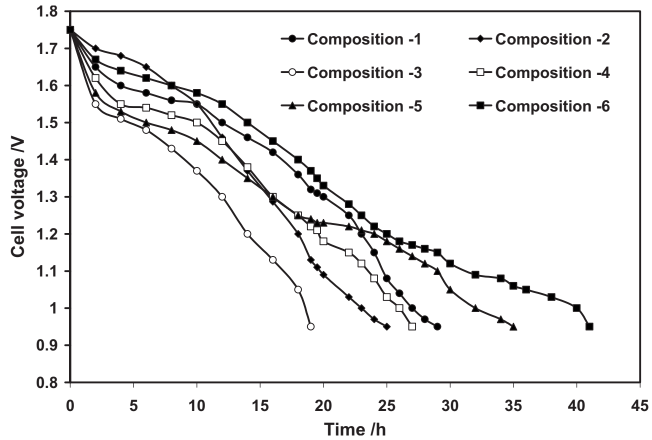

Figure 1. Discharge behavior of Al/MnO_2 cells with different compositions of electrolyte mixture ($AlCl_3$ + $CrCl_{3+}NH_4Cl$) at a constant current drain of 100 mA.

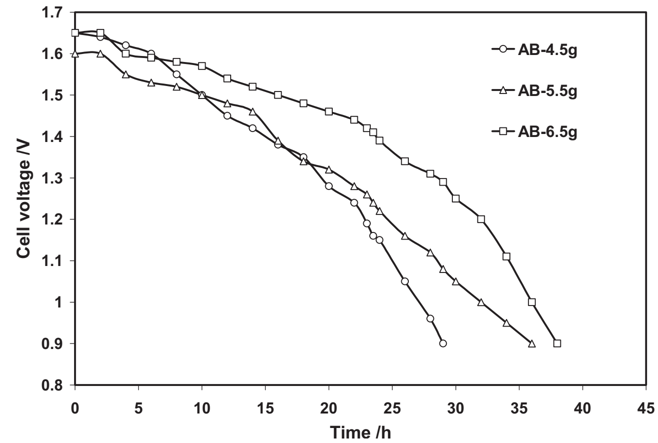

Figure 2. Discharge behavior of Al/MnO_2 cells with different concentrations (wt %) of AB at a constant current drain of 100 mA.

ibility and elasticity to the cathode bobbin mix. In addition, AB-containing cells usually give superior intermittent service, which is the way most dry cells are used. Graphite serves better for high flash currents or for continuous drains. In the present investigation, the AB content was optimized by varying its content from 4.5 to 6.5 g in the cathode bobbin mix through discharge studies carried out at 100 mA current drain. However, it was found that further increasing the AB quantity increases the bulk volume of the active mix, as it could not be accommodated in the can. The cells employed an electrolyte composition of 6, i.e., $AlCl_3$; (3 g) + NH_4Cl; (1.5 g) + $CrCl_3$; (1 g) with a binder contents amounting to 5% binder.

Discharge studies.— Constant current discharge studies of Al/MnO_2 dry cells were carried out using an in-house made battery tester for optimizing AB content, electrolyte composition, and evaluating cell characteristics at ambient and high temperatures (50 and 60°C). Two varieties of aluminum were studied. One is 2S aluminum (commercial grade) and magnesium-rich aluminum (2% Mg) with an idea to improve the cell operating voltage.

Results and Discussion

Optimization of electrolyte.— Figure 1 shows the discharge behavior of Al/MnO_2 dry cells prepared with a different composition of electrolyte in the bobbin mix and discharged at a constant current drain of 100 mA. The basic constituents in the electrolyte are aluminum chloride, ammonium chloride, and chromium chloride. Aluminum chloride was used mainly for the supply of aluminum ions. Its pH was found to be in the range of 2–3. Ammonium chloride was used to raise the pH to the range of 4–5 in which the potential of EMD is maximum. Chromium chloride is added to provide corrosion inhibition when the cell is not in use. The average pH of the electrolyte was maintained at or near 4.7.[7,8] It can be seen that (Fig. 2) the Al/MnO_2 cell with electrolyte composition of 6 [$AlCl_3$; (3 g) + NH_4Cl; (1.5 g) + $CrCl_3$; (1 g)] has delivered superior performance (4.2 Ah corresponding to a coulombic efficiency of 85.7%) when compared to other compositions. Hence, this composition was selected as optimum and used in the dry cells prepared for further investigations. The superior performance may be associated with the better properties related to ionic conductivity and high dissociation of charges at this concentration. However, the studies related to the transport properties and dissociation constants, etc. to understand its functionality are in progress.

Optimization of AB.— Figure 2 shows the discharge behavior of Al/MnO_2 dry cells prepared with varying AB content (4.5, 5.5, and 6.5 g) in the bobbin mix and discharged at a constant current drain of 100 mA. The discharge capacities obtained for Al/MnO_2 dry cells with 4.5, 5.5, and 6.5 g of AB are 2.9, 3.6, and 3.9 Ah, respectively. It is evident that cells with 6.5 g AB exhibit a superior performance (3.9 Ah). Further, it can be seen that a marginal increase in the open-circuit voltage (OCV) is observed with an increase in AB content. Hence, it is confirmed that a higher AB content facilitates the electrochemical cell performance of the dry cell by formation of a chainlike network with better water retention, thereby reducing the internal resistance and high electrical conductivity of the cathode bobbin.

Electrochemical performance.— Figure 3 shows room-temperature discharge studies of Al/MnO_2 dry cells (employing 2S and AM alloys as the anode) at different current drains, viz., 100, 200, 300, and 400 mA. It is evident that cells employing 2S aluminum alloy as the anode show a higher OCV of 1.75 and outperform AM alloy at all current drains. 2S aluminum alloy cells deliver 4.2 Ah at 100 mA current drain while the cells with AM alloy counterpart deliver 2.4 Ah, which is nearly 50% lower than the cells of 2S alloy. Indeed, the superior performance of 2S alloy may be attributed to the high purity of aluminum (99%). Further, it is apparent that the alloying of magnesium (2%) with aluminum at low concentration was not beneficial either in improving the potential or the capacity.

Performance of Al/MnO_2 dry cells at elevated temperatures.— Figure 4 shows the discharge behavior of 2S alloy Al/MnO_2 dry

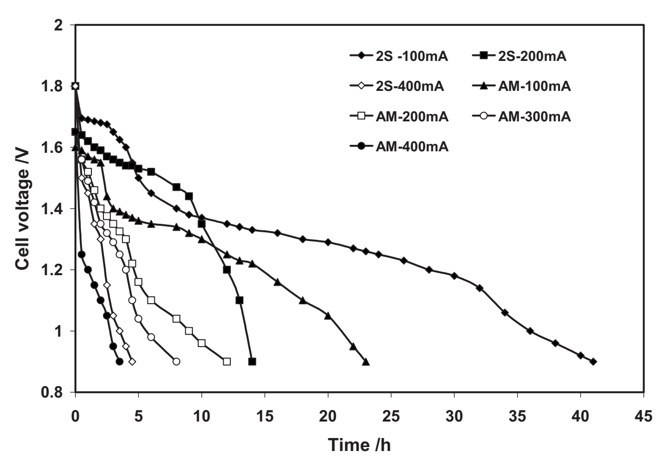

Figure 3. Discharge characteristics of Al/MnO_2 dry cells (employing 2S alloy and Al–Mg alloy as the anode) at different current drains, viz., 100, 200, 300, and 400 mA.

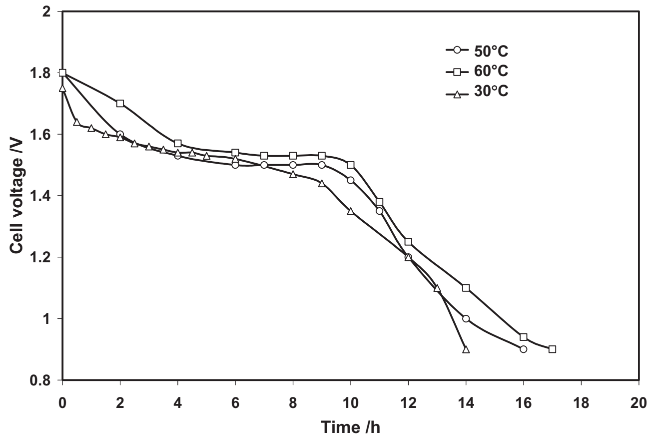

Figure 4. Discharge behavior of Al/MnO_2 dry cells (employing 2S alloy) at elevated temperatures, viz., 30, 50, and 60°C at a constant current drain of 200 mA.

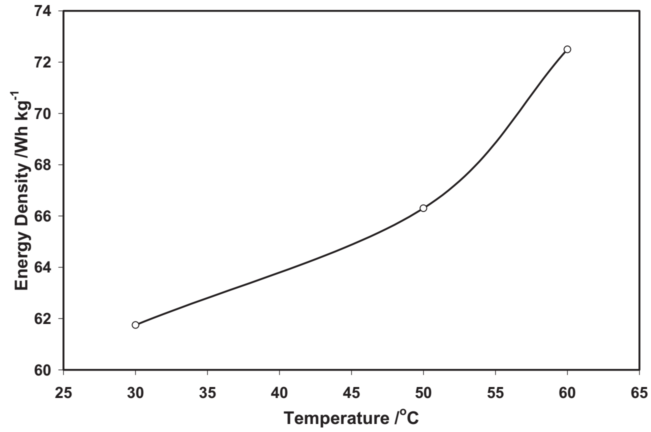

Figure 6. Effect of operating temperature (30, 50, and 60°C) on energy density characteristics of Al/MnO_2 dry cells (employing 2S alloy).

cells at 30, 50, and 60°C at a constant current drain of 200 mA. The discharge performance of the cells increases with an increase in operating temperature. The cells discharged at 60°C exhibited 3.4 Ah, which is 12% more than the room-temperature performance (2.8 Ah). The cells discharged at 50°C delivered 3.2 Ah. An increase in the operating potential is also observed by 0.3 V. The higher performance may be attributed to the enhancement in the transport properties of the electrolyte. Further, it can be seen that the voltage profile reflects a plateau region around 1.5 V assignable to the reduction of MnO_2.

A comparative performance of Al/MnO_2 and Zn/MnO_2 dry cells discharged at 100 and 200 mA current drains is shown in Fig. 5. It can be clearly seen that the voltage characteristics of Al dry cells are higher than Zn cells by ~0.3 V at 200 mA current drain. This suggests that Al dry cells can offer higher energy and power density characteristics as compared to their Zn counterpart.

Figure 6 shows the variation of energy density of 2S alloy Al/MnO_2 dry cells at different temperatures, viz., 30, 50, and 60°C. It can be seen that the energy density increases with an increase in temperature up to 60°C. The cells exhibit an energy density of 73 Wh kg^{-1} at 60°C and the same is obtained at 61 Wh kg^{-1} at ambient temperature.

Performance of Al/MnO_2 dry cells on storage.— Figure 7 shows OCV characteristics of Al/MnO_2 dry cells employing 2S alloy and AM alloy for a period of 40 days. Both the cells maintain their OCV over the tested 40 days without much variation. In the case of 2S alloy a first decrease in the OCV was observed after 20 days and the next fall was after 30 days. However, the fall was of the order of 0.01 V. In the case of AM alloy the drop in the OCV was observed after the 17th and 34th days and the drop was to the tune of 0.01 V, corroborating the readiness of the dry cells for service. The discharge performance of the aluminum dry cells was evaluated at 100 mA current drain after 40 days of storage at ambient temperature (Fig. 8). The cells exhibit a performance fairly similar to that of freshly assembled ones. Over the 40 days of storage, cells employing 2S aluminum delivered 4.1 Ah while the AM cells exhibited 2.2 Ah, which corresponds to a 0.02 and 0.08% reduction in capacity, respectively. Further, the cells did not reflect practically any voltage delay. Though these results are very much indicative, further investigations are underway. An extensive evaluation of shelf-life characteristics and field worthiness for consumer applications of Al/MnO_2 dry cells shall be reported in our subsequent articles.

Conclusion

Al/MnO_2 dry cells have been investigated to use as an attractive alternative to Lechlanche and Mg/MnO_2 dry cells toward consumer applications in the light of economics. Two grades of aluminum

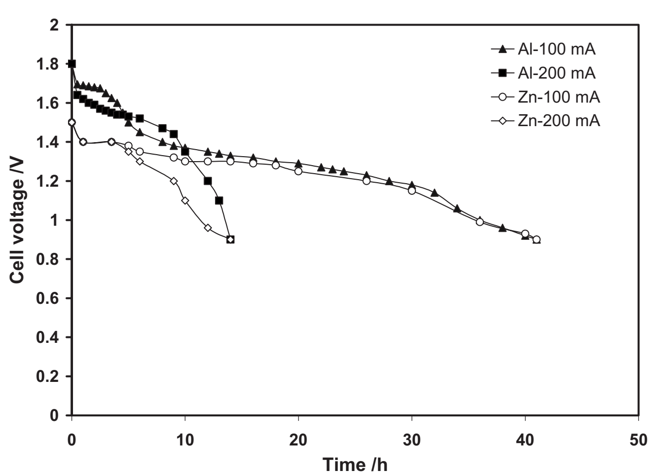

Figure 5. Discharge behavior of Al/MnO_2 and Zn/MnO_2 cells at 100 and 200 mA current drains.

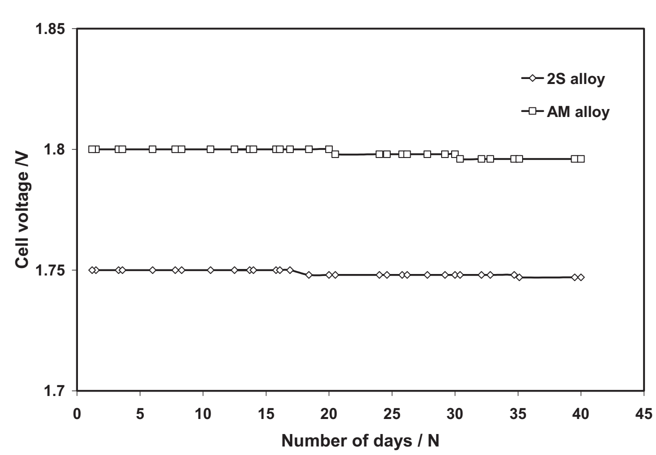

Figure 7. OCV retention of Al/MnO_2 dry cells employing 2S alloy and AM alloy for a period of 40 days.

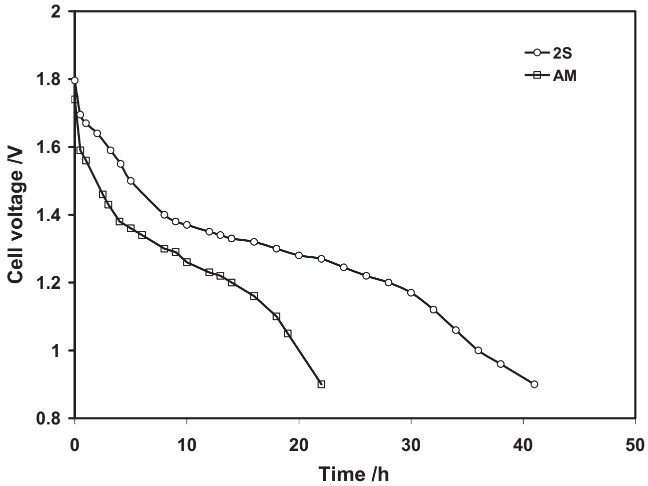

Figure 8. Discharge behavior of Al/MnO_2 dry cells employing 2S alloy and AM alloy 100 mA current drain after 40 days of storage.

[aluminum 2S alloy sheets (commercial), aluminum–magnesium alloy (in-house made)] were used. The optimization of AB, electrolyte composition, and electrochemical behavior of Al/MnO_2 dry cells was investigated comprehensively and the results are optimistic. Al/MnO_2 cells employing 2S aluminum anode deliver 4.2 Ah at 100 mA current drain corresponding to a coulombic efficiency of 85% and behave better at elevated temperatures.

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References

1. R. Jasinski, *High Energy Batteries*, Plenum Press, New York (1967).
2. J. L. Robinson, in *The Primary Battery, Vol. II*, N. C. Cahoon and G. W. Heise, Editors, p. 149, Wiley, New York (1976).
3. S. Ruben, U.S. Pat. 2,481,359 (1949).
4. S. Zaromb, *J. Electrochem. Soc.*, **109**, 1125 (1962).
5. Y. Yokota, *Denki Kagaku*, **28**, CA 62: 2503b (1960).
6. D. Linden and T. B. Reddy, *Handbook of Batteries*, 3rd ed., McGraw-Hills International, New York (2001).
7. H. Robinson, *Corrosion (Houston)*, **2**, 199 (1946).
8. J. Stokes, in *The Electrochemical Society Meeting*, Pittsburgh, October (1955).