Transactions of the SAEST Vol. 22, No. 3, 1987

STUDIES ON MANGANESE DIOXIDE FOR RECHARGEABLE ALKALINE CELLS

R. Ilangovan, B. Manivannan and K. Dakshinamurthi

Central Electrochemical Research Institute Madras Unit, CSIR Complex,
Madras 600 113

Abstract : A comparative study of natural and electrolytic manganese dioxide used in rechargeable alkaline cells is presented. The effect of physical parameters on the addition of graphite to improve the conductivity of MnO_2 and the performance of cells fabricated with such MnO_2 samples are discussed.

INTRODUCTION

Alkaline manganese dioxide battery system was rediscovered and put to commercial use in 1960s almost 100 years after the first report. The system has an edge over the conventional dry cell in continuous high drain applications, in rechargeability and in extended storage and low temperature applications. It is consumed to the extent of 20% of dry cell market in USA and Japan and is being marketted almost all over the globe. The system is ideally suited for small computers, TV and movie cameras, electric shavers, casette tape recorders, electric typewriters, hand tools, portable TV and other high drain electronic applications. In India, it has yet to make its debut. The Indian consumption of dry cell is of the order of 1.5 cell per capita which is bound to go up. If even part of the market especially in consumer electronics (gadgets using high drain batteries) is satisfied by alkaline manganese dioxide system, the demand is bound to be substantial.

The trend in the use of manganese dioxide has shifted from natural ore (NMD) to electrolytic (EMD) and chemical varieties (CMD) both due to better performance of the latter and reduced arrivals of good quality ore of the former. In the case of rechargeable alkaline cells, it has been established that only gamma variety of MnO_2 is suitable and that too the performance is in the following order. [1]

$$\text{EMD} > \text{CMD} > \text{NMD (African)}$$

The desirable physical and chemical properties for efficient battery functions especially rechargeability are not clearly established. However, as these properties vary from sample to sample, from different sources, it is necessary to study these properties, for comparing notes and performance.

Paper presented at the 5th National Conference on Power Sources, Batteries & Fuel Cells held at Bangalore on 18-19, August 1986

0036 – 0678 / 87 / 2203 – 0127 $ 2-00 /

The present communication disribes the studies on natural and electrolytic MnO_2 in alkaline cells and the rechargeability features. Details of physical properties, electrical resistivity studies and cell performance are reported here.

EXPERIMENTAL

NMD employed was African ore type provided by Messrs. Union Carbide, Madras, while EMD was of CECRI make. The physical and chemical properties have been measured as per established procedures. The pH value in distilled water (US specification, and half cell potential in KOH solution were measured. The electrical resistivity has been measured using procedure similar to that used by F. G Fischer *et. al* [2], but using DC current flow and monitoring potential drop. Electrical resistivity of MnO_2 without addition of graphite and with different composite additions at various compaction pressures have been carried out.

The studies here are confined to flat plate prismatic cells. Nickel plated mild steel mesh grid was used for MnO_2 electrode while, for zinc powder-compact electrode, galvanised m.s. grid was used. Details are as given below:

Electrode size	: 10 × 5cm²
Apparent surface area	: 100 cm²/electrode
Cathode active material	: 20 g/electrode
Anode	: 25 g/electrode
Quantity of (40%) electrolyte	: 60ml
Container	: Perspex
Cell overall weight	: 250 g

The compressed flat plate electrodes were covered with 5 layers of cellophane separator and each MnO_2 electrode was flanked by two zinc electrodes. The cells were subjected to usually continuous drains, always terminating the discharge at 1.0V, whatever was the rate of discharge. Cycling experiments were carried out at 100% depth of discharge (DOD) to 1.0V cut off, charge and discharge current kept at 100 mA drain. Charging voltage was restricted to 1.75V. For cycling experiment at various DOD an electroinc automatic cycling unit has been designed and fabricated.

RESULTS AND DISCUSSION

Table I gives the properties of the NMD and EMD employed in this investigation. The properties compare favourably with those reported in literature [3] for these types. From the table, it is seen, of the two samhles employed by us, EMD has larger surface area and smaller partticle size therby indicating its better suitability for our purpose. Both the varieties are supposed to be of Gamma type and expected to perform in the cell in the same way *i. e.*, by addition of proton and electron and lattice expansion during discharge. Subsequent results indicate the better performance of EMD

TABLE I

PROPERTIES OF MANGANESE DIOXIDE

Property studied	Literature (Typical)		Experimental samples	
	NMD	EMD	NMD	EMD
Surface area (ZIA method) m²/gm	8.9	40.8	24.5	28.0
Sieve analysis (%)				
+50	Trace	—	Trace	—
— 50 to + 100	42.3	Trace	30.0	—
— 100 to + 200	28.6	11.2	40.0	—
— 200 to 300	—	31.4	14.0	—
— 300	12.2	—	14.0	100.0
— 350	16.8	57.4	—	—
Tap density (gm/cc)	2.47	2.22	2.30	1.90
pH (distilled water)	3.75	2.92	5.78	4.72
Half cell potential in 40% KOH (V)	—	—	0.20	0.14
Electrical resistivity Ω cm	—	—	600.0	60.0
Compactability	—	—	Good	Fair
Moisture content (%)	1.24	1.44	2.0	1.4

Electrical resistivity studies :

In Fig. 1, the results of the effect of compacting pressure on electrical resistivity for NMD and EMD with and without addions of graphite powder are presented. In the case of EMD, the studies were on the bare material and with 25% graphite powder. In the case of NMD, apart from the ore alone, effect of graphite concentration from 5 to 25% are presentented. The results show that as compacting pressure is increased the resistance of the material decreases, as is expected. However it reaches a saturation value around 0.5 to 1.0 T/cm². The electrical resistivity of EMD without additions of graphite powder (60Ωcm) is one order lower than that of NMD (600Ωcm) at the saturation compacting pressure. The resistance of NMD is progressively lowered with increase in concentration of graphite level and reaches optimum values (around 1Ωcm or lower) at 10 to 25% concentration. EMD with 25%

graphite addition has comparable resistance to NMD with similar additions of graphite. The variation for different graphite concentration in electrical resistance is presented in Table II.

TABLE II

SATURATION ELECTRICAL RESISTANCE (MEASURED)

Percentage of Graphite	EMD		—		NMD		
	0%	25%	0%	5%	10%	20%	25%
Electrical Resistivity at saturation compacting pressure (Ω–cm)	60	0.25	600	10	0.6	0.15	0.10

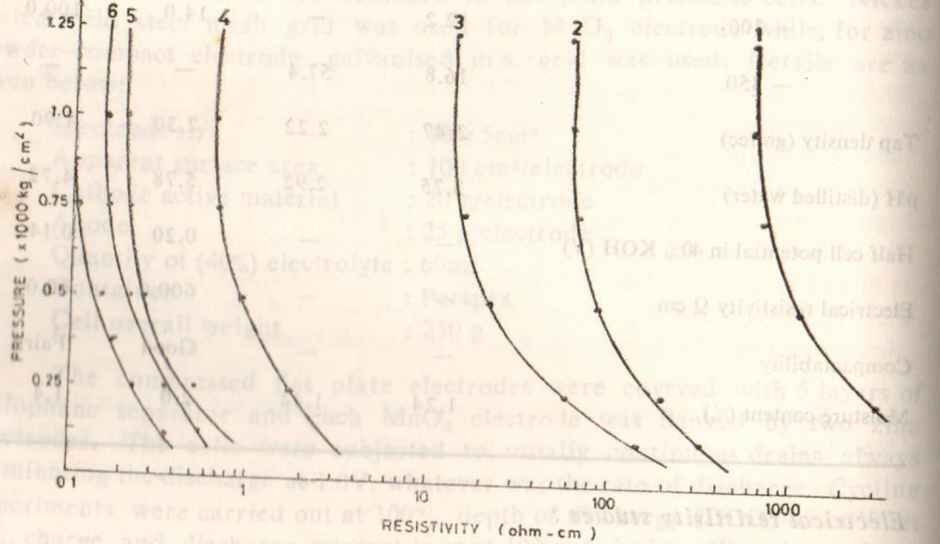

Fig. 1 Effect of compacting pressure on resistivity

1 NMD alone
2 EMD alone
3 NMD + 5% graphite
4 NMD + 10% graphite
5 NMD + 20% graphite
6 NMD + 25% graphite

In the case of NMD, 10% graphite addition substantially reduces the electrical resistance at saturation compacting pressure. Therefore, 10–25% graphite concentration seems to be optimum, the proportion varying depending on applications. Fig 2. clearly indicates that as graphite concentration increrses, resistance decreases and almost reaches a steady value. The figure also cleary shows that further compacting pressure will have no significant contribution in bringing down resistance. Fig 3. shows the influence of particle size on resistivity at various compacting pressures for NMD with no graphite addition. The resistance values are more or less in the same range with minor variations due to particle size. Increased particle size slightly increases the resistance. With graphite (25%) addition, it is seen in Fig 4. that conductivity increases with increase in particle size substantially at lower compacting pressure. At higher pressures the conductvity variation with particle size is not significant thereby indicating that particle size has no effect atleast as far resistance of the composite is considerd. However surface area considerations still require finer particle size of better electrical performance. Fig. 5 shows the intial and first cycle discharge capacity variation of NMD electrodes at various graphite concentrations. This brings out the fact that graphite concentration is optimum at 15 to 25% as is established by electrical resistance measurement.

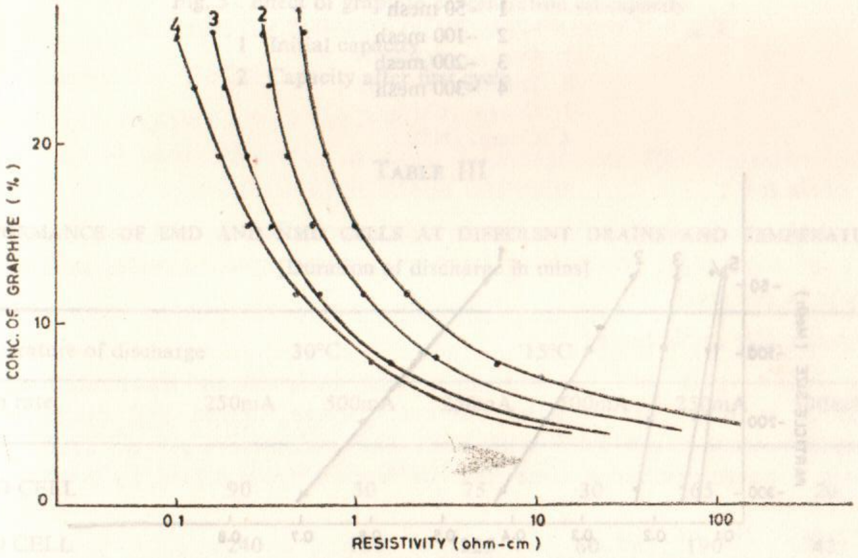

Fig. 2 Effect of graphite concentration on resistivity

1 0.125 Ton/cm²
2 0.25 Ton/cm²
3 0.5 Ton/cm²
4 0.75 Ton/cm²

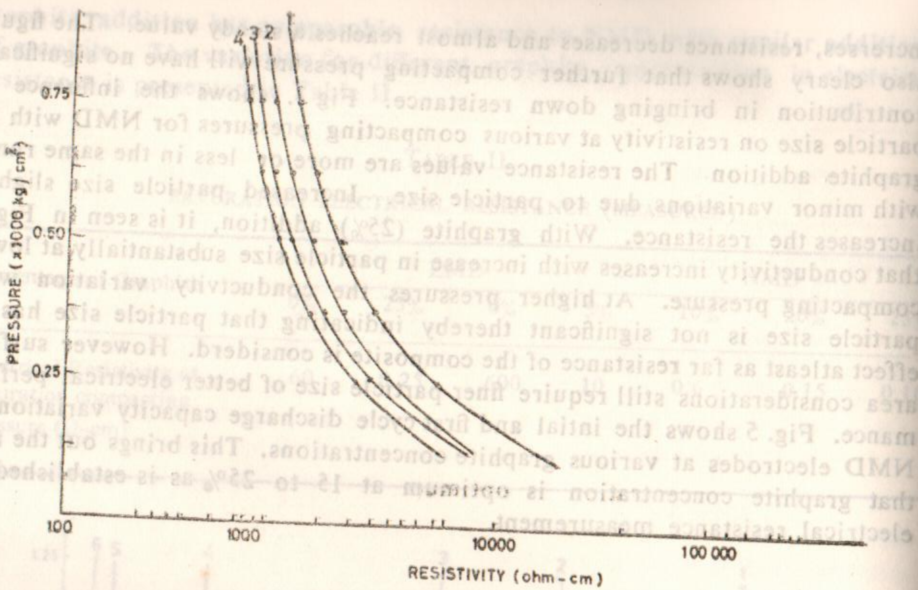

Fig. 3 Effect of compacting pressure on resistivity of MnO_2 for various particle sizes

1 -50 mesh
2 -100 mesh
3 -200 mesh
4 -300 mesh

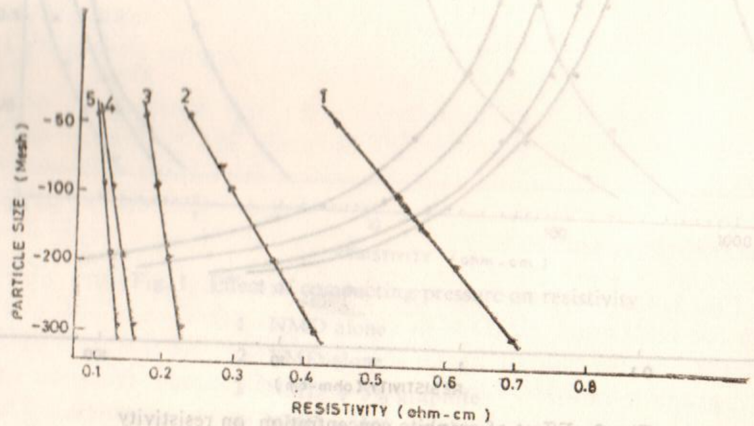

Fig. 4 Effect of particle size on resistivity of MnO_2 + 25% graphite for various compacting pressures

1 0.125 Ton/cm²
2 0.25 Ton/cm²
3 0.5 Ton/cm²
4 0.75 Ton/cm²
5 1 Ton/cm²

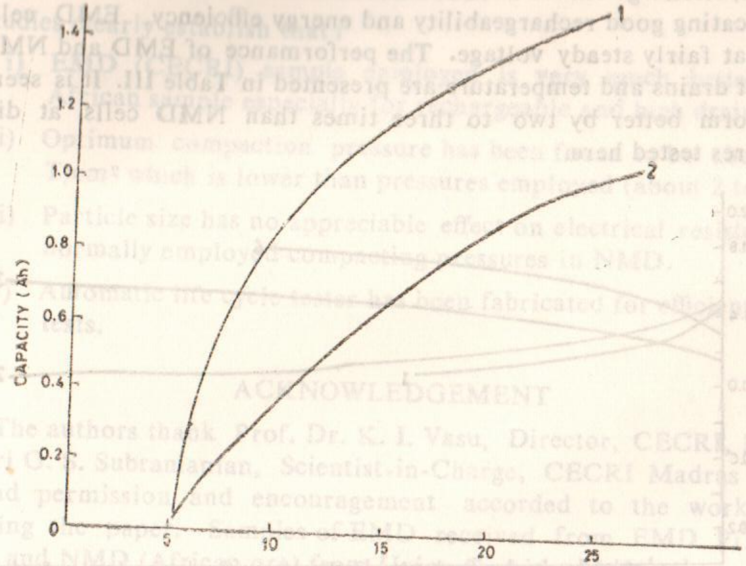

Fig. 5 Effect of graphite concentration on capacity

1 Initial capacity
2 Capacity after first cycle

TABLE III

PERFORMANCE OF EMD AND NMD CELLS AT DIFFERENT DRAINS AND TEMPERATURES
[Duration of discharge in mins]

Temperature of discharge	30°C		15°C		5°C	
Drain rate	250mA	500mA	250mA	500mA	250mA	500mA
NMD CELL	90	30	75	30	65	20
EMD CELL	240	100	225	60	190	42

Performance of prismatic cells:

Fig. 6 shows the charge discharge behavior of flat plate cells using NMD and EMD active material. While NMD cell gave about one ampere hour capacity, EMD performed very much better at the same rate (100mA) to give 3 times capacity. NMD cells show a lower discharge plateau and also higher charge plateau thereby indicating their inferiority to EMD cells

The charge/discharge curves at this current drain are very close in the case of EMD indicating good rechargeability and energy efficiency. EMD cells also discharge at fairly steady voltage. The performance of EMD and NMD cells at different drains and temperature are presented in Table III. It is seen EMD cells perform better by two to three times than NMD cells at different temperatures tested here.

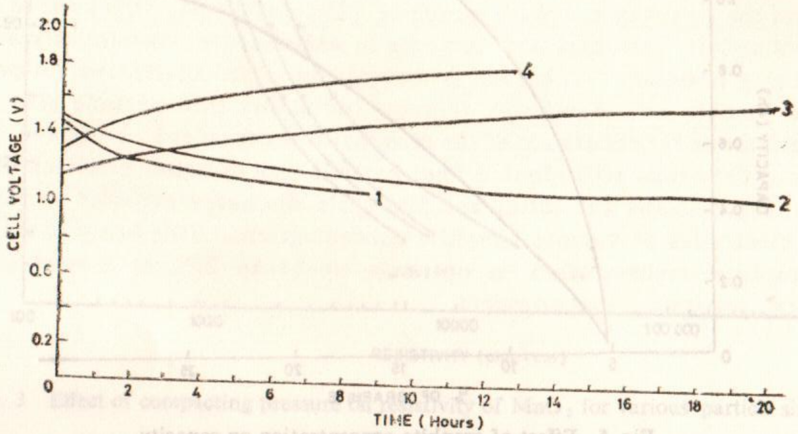

Fig. 6 Charge/discharge curves of NMD/EMD electrodes

1 Discharge (NMD)
2 Discharge (EMD)
3 Charge (EMD)
4 Charge (NMD)

Life cycle test :

Life cycle studies have been carried out on few NMD cells at 100% depth of discharge, trials have been completed upto 10 cycles and further work is in progress.

Automatic life cycle tests :

A life cycle unit has been specially designed and fabricated so that charging is done at constant current voltage limited and discharge at constant current below 1.5V with both the parameters set on front panel control. Charge/discharge time can be varied from 0.1sec. to 999 hours.

Features : No. of cells : 4
Charger : CCVL (0-1 A, 1-2V/cell)
Discharge : CC (0-1 A)
Discharge cut off : 0-2V/cell
Timer : Charge/discharge (secs to hours)
Cycles indicator : 3 digit with preset cycle cut off

This Unit can test the batteries faster and efficiently especially for life cycle testing. A detailed performance trials with this equipment at different DOD and temperature will be communicated subsequently.

CONCLUSION

The studies clearly establish that :

i) EMD (CECRI) sample employed is very much better than the African sample especially for rechargeable and high drain purposes.

ii) Optimum compaction pressure has been found to be about 0.6 to 1 T/cm^2 which is lower than pressures employed (about 2 to 3 T/cm^2).

iii) Particle size has no appreciable effect on electrical resistance at the normally employed compacting pressures in NMD.

iv) Automatic life cycle tester has been fabricated for efficient life cycle tests.

ACKNOWLEDGEMENT

The authors thank Prof. Dr. K. I. Vasu, Director, CECRI, Karaikudi and Shri G. S. Subramanian, Scientist-in-Charge, CECRI Madras Unit, for the kind permission and encouragement accorded to the work and for presenting the paper. Samples of EMD received from EMD Pilot Plant, CECRI and NMD (African ore) from Union Carbide, Madras, are gratefully acknowledged.

DISCUSSION

C. Chakkaravarthy, CECRI

Q. What is the cycle life of the MnO_2 cell?

A. Normally about 25 cycles in deep discharge and 200 in shallow cycles. We have yet to establish cycle life of our cells.

Q. What is the charge – discharge efficiency?

A. At controlled conditions, above 90%

Q. What is the separator? Is it limiting the cycle life?

A. We have used cllophane and have not diagonised failure modes since cycling studies are at preliminary stages.

K. J. Sethuraman, LRDE, Bangalore

Q. Have you tried the cylindrical configuration?

A. Not yet.

Q. Will not assembly and construction of cylindrical easier than prismatic cells?

A. For mass production, cylindrical cells have proved advantageous.

REFERENCES

1 R Chemelli, J Gsellmann, G Korbler and K Kordesch, *Manganese dioxide Symposium Vol 2. Electrochem Soc* Inc. (1980) p 150-160

2 F G Fischer and M Wissler, *ibid* p 711-717

3 Y Uetani, T Iwamaru, Y Ishikawa, N Maekawa and K Tani *ibid* p 11-15