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A NEW CELL FOR ELECTROCHEMICAL CHARACTERISATION OF MANGANESE DIOXIDE FOR ALKALINE BATTERIES

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A new nickel plated mild steel cell with inner dimensions of LR6 cell and with a detachable bottom plug has been designed for the evaluation of manganese dioxide particularly for alkaline cells. The technique has been standardized for rapid evaluation, by optimising graphite content, at a discharge current of 125 mA.g^{-1} simulating 1 Ω load of LR6 cell. The cell can be used for evaluation of other active materials and also for characterisation of MnO_2 with respect to compactibility, conductivity, porosity, density, volume change in electrolyte and alkali absorption.

Key words: Manganese dioxide, alkaline batteries, electrochemical characterisation

INTRODUCTION

Various cells [1-5] employing different conditions have been adopted for the day-to-day evaluation of manganese dioxide. Plastic cells have been predominantly used at low current drain with platinum or zinc anodes with or without reference electrodes. The graphite content in the cathode mix ranges from 3 to 10 times the weight of MnO_2. In actual practice, graphite content ranges from 0.1 to 0.15 times the weight of MnO_2. The details of the thickness, area and compaction pressures of the MnO_2 cake as well as the cell design are not available in the reported cases cited. Some have used zinc gel anodes also in the cell. This paper reports electrochemical characterization studies on MnO_2 that nearly simulates the conditions of LR6 cells at high discharge rate.

EXPERIMENTAL

The details of the cell are presented in Fig. 1. The cell was nickel plated (2-3 μm) including the detachable plug. The cathode mix (0.2 g electrolytic MnO_2 + graphite) moistened with potassium hydroxide (1 ml of 30%) was fed into the cell and compressed at an optimised pressure [6] of 0.6 ton. cm^{-2} with a punch. Zinc gel anode (4 g) in a kuralon separator cup was used as the anode with copper lead. The cell was discharged, 15–30 minutes after fabrication, at constant current. The physical dimensions of the pellet were measured at different graphite ratios by pressing out the pellets. Electrolytic MnO_2 (EMD) used in the experiments was of Indian origin. Performance of IBA 18 also was studied. As large surface area zinc powder gel anode was employed, no reference electrode was used and the potential of zinc remained nonvariant (capacity ratio MnO_2 : Zn = 1:52). Each experiment was carried out three times per sample and reproducible results were obtained.

RESULTS AND DISCUSSION

Features of the electrochemical cells for evaluation of MnO_2 are given in Table I. A typical discharge curve for EMD sample is presented in Fig. 2. There are two discharge plateaus and the capacity calculation have been confined to cut off voltage of 1.0 V (one-electron discharge state).

Effect of graphite content in cathode pellet

The effect of graphite addition in the cathode pellet has been studied in ratios ranging from 1 to 10 times the amount of MnO_2. The results are presented in Table II. It is seen from the discharge duration at 125 mA.g^{-1} drain that 1:1 ratio is the best. At the ratio of 1:0.1, the discharge starts at less than 1.0 V and therefore this ratio has been

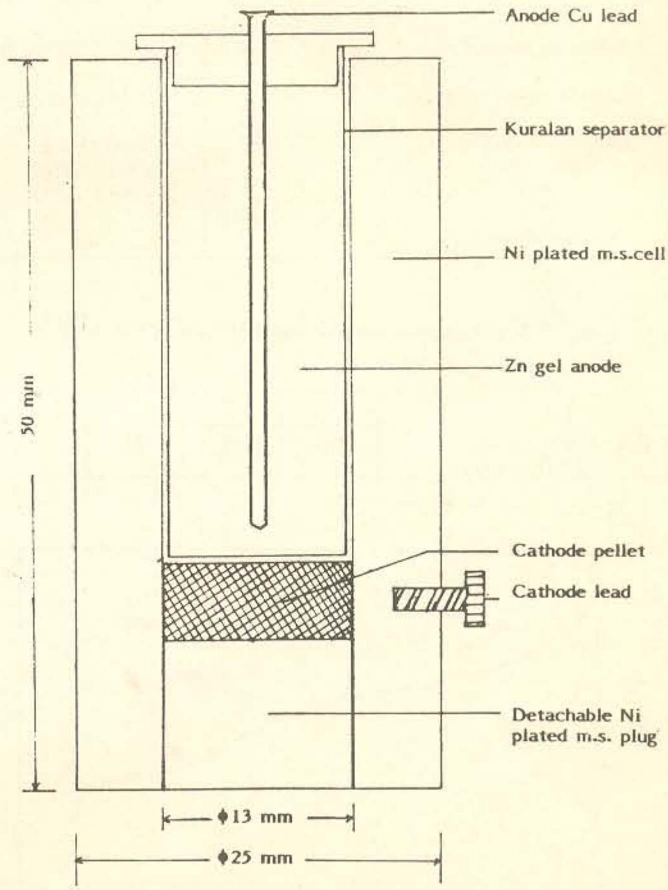

Fig. 1: Electrochemical cell for evaluation of MnO_2

found to be not suitable for the studies in the cell. Therefore 1:1 ratio has been adopted for further studies.

Effect of cathode pellet thickness

The physical dimension of the cathode pellet is presented in Table III at different graphite ratios. It is seen from the Table that at 1:1 ratio the pellet thickness is 1.80 mm which is very close to the actual cathode thickness in LR6 cell (2.20 mm). Therefore, study at this cake thickness simulates actual LR6 cell conditions. The variation of duration of discharge with pellet thickness also establishes that 1:1

TABLE-I: Features of electrochemical cells for evaluation of MnO_2

1	2	3	4	5
Features	A Kozawa [1] cell	Kerr-McGee [2] (Standard test) cell	Mitsui [3] cell	CECRI cell
Cathode :				
Quantity of MnO_2 per expt. (g)	·0.1	1	No information	0.2
MnO_2 : Graphite	1 : 10 (: 20) (coke)	1 : 3	"	1 : 1
Apparent area (cm^2)	4.91	No information	"	1.33
Thickness (cm)	· 0.8	0.5	"	0..18
Pressure applied ($T.cm^{-2}$)	Not defined	No information	"	0.6
Separator	Paper	Paper	Vinylon cup	Kuralon
Anode	Pt wire	Zn coil	Zn–Hg powder with Pt wire lead	Zn–Hg gel
Electrolyte	KOH (or) $ZnCl_2$ / NH_4Cl	KOH	KOH	KOH
Material of construction of cell	Plastic	Plastic steel	Hard PVC with Ni rod lead	Ni plated m.s. with pull out plug
Reference electrode	Hg / HgO (or) SCE	None	None	None
Current drain ($mA.g^{-1}$)	10 and 20	10 and 20	Load 10, 20 and 40 Ω	1.25
Cut off voltage (V)	– 0.20 and – 0.40 vs HgO – 0.0 V vs SCE	0.34 vs HgO (1.0 V vs Zn)	0.9	1.0 V vs Zn
Duration of test (h)	48	12	3–18	3

TABLE-II: Effect of graphite content (current drain of 125 $mA.g^{-1}$)

	MnO_2 : graphite ratio			
	1 : 1	1 : 3	1 : 5	1 : 10
Discharge duration upto 1.0 V (minutes)	108	94	90	86

TABLE -III: Physical dimensions of cathode pellet at different graphic additions

Pellet diameter : 1.30 cm   Pellet area : 1.33 cm^2

	MnO_2 : graphite ratio			
	1 : 1	1 : 3	1 : 5	1 : 10
Pellet weight (g)	0.49	0.96	1.26	2.67
Pellet thickness (mm)	1.80	3.70	5.20	11.00

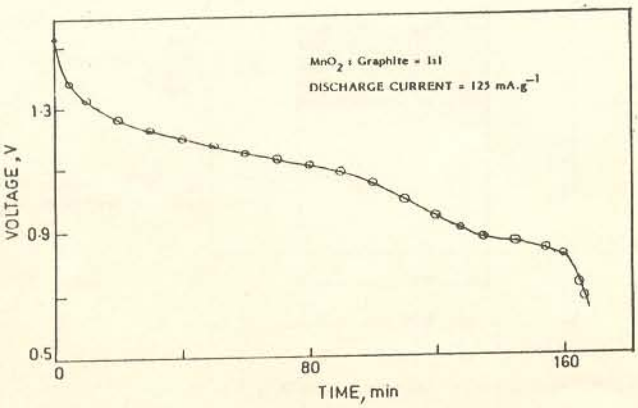

Fig. 2 : Discharge curve of EMD

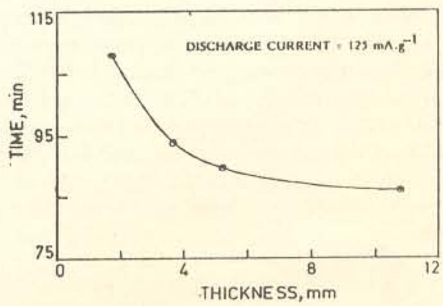

Fig. 3 : Variation of duration of discharge of EMD with thickness of pellet

ratio is the best for estimating MnO_2 samples (Fig. 3). The apparent surface area of the cathode pellet is 1.33 cm^2 and is about 12% of the geometric surface area of the cathode in LR6 cell. The current drain in the test cell is therefore one order higher with respect to the apparent area in actual LR6 cell.

Effect of current drain

From separate discharge studies on a number of commercial LR6 cells, the average peak discharge current at 1Ω load has been found to be 0.95A and for a MnO_2 content of the cell at 7.5 g, the current drain is 125 $mA.g^{-1}$. This current drain is employed for evaluation of MnO_2 in this paper for the rapid estimation of the electrochemical activity. However, the effect of other current drains ranging from 50 to 250 $mA.g^{-1}$ has been studied and their performances are presented in Table IV. It is seen that an efficiency of about 81% is achieved at 125 $mA.g^{-1}$ current drain for the sample employed and at lower current range. For IBA 18 sample, the discharge duration at this current drain is 120 minutes (i.e. material efficiency of 88%).

TABLE-IV: **Effect of current drain (MnO_2 : graphite = 1 : 1)**

Cell current (mA)	Duration of discharge upto 1.0 V (minutes)	Total capacity ($mA.mm^{-1}$)	Material efficiency* (%)
50	30	1500	45.0
25	108	2700	81.2
10	270	2700	81.2

* For 90% MnO_2 content.

CONCLUSION

From the results presented, the best conditions for electrochemical characterisation of MnO_2 for alkaline cell using the designed cell are as given in Table I (column 5). The advantages of the cell and the technique are as follows :

(i) Rapid and reproducible evaluation of MnO_2 samples, (ii) High current drain simulation studies, (iii) Same cell/technique can be used for other MnO_2 cells ($ZnCl_2$ or lithium systems) or other active material with minor modifications.

Apart from electrochemical characterisation by the cell, the physical pull out of the cathode pellet facilitates the evaluation of (a) pellet density (b) porosity of pellet (c) compactability of cathode active material (d) volume changes due to alkali soak (e) electrolyte absorption and (f) conductivity of the cathode pellet.

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