

## PERFORMANCE OF LITHIUM CELLS WITH ELECTROLYTIC MANGANESE DIOXIDE

R JANAKIRAMAN, P N N NAMBOODRI and R GANGADHARAN

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

The effect of heating the electrolytic manganese dioxide (EMD) obtained from the Indian ore on the performance of Li/MnO button cells has been investigated. Portions of the MnO samples were heated to 373K, 573K and 1023K respectively. Lithium perchlorate solutions in propylene carbonate of concentrations 0.5M, 1M, 1.5M and 2M were used as electrolyte solution. Button cells of 20 mm dia. were fabricated with each MnO sample and with the different concentrations of electrolyte solution. Cellulose material was used as separator. Cells were also assembled with mixed solvents of propylene carbonate and dimethoxy ethane.

These cells were discharged at 50A, 100A and 200A. The internal resistances of these cells have been determined. It was observed that the MnO sample heated at 573K with one molar lithium perchlorate solution in propylene carbonate gave the best performance.

**Key words:** Electrolytic MnO, heating effect, improvement in lithium cells

### INTRODUCTION

Considerable amount of work has been done to correlate the effect of heating MnO<sub>2</sub> on its properties and performance characteristics. By heating MnO<sub>2</sub>, the occluded water in it is removed. As a result, the crystal structure of the dehydrated MnO<sub>2</sub> is changed. Hence, change in its performance is to be expected. The combined water promotes the movement of protons in the solid phase [1]. It has been observed [2] that  $\gamma$ -MnO<sub>2</sub> may change to  $\beta$  MnO<sub>2</sub> when heated to 673K. A large number of research papers have been published on the electrochemical activity of various manganese dioxides heated at different temperatures [3,8]. EMD heated to 473K, 673K, 873K and 1073K has been discharged [7]. Release of combined water of MnO<sub>2</sub> was studied mass spectroscopically (in vacuo) ranging from room temperature to 773K at increments of 373K [9] and it was concluded that the geometry of dehydrated patterns obtained was characteristic of the types or sources of MnO<sub>2</sub>. It was proved that the MnO<sub>2</sub> with plural water release peaks a 473K and 573K exhibited excellent battery performance.  $\gamma$ -MnO<sub>2</sub> upon heating from 473 to 673K transformed smoothly to pyrolusite [10,11].

The effect of heating MnO<sub>2</sub> on their discharge performance has been studied [12]. The relation between heating temperature and X-ray diffraction patterns has been reported by many researchers [13,14]. MnO<sub>2</sub> showed  $\gamma$ -phase between room temperature and 523K,  $\gamma\beta$ -phase between 523-623K and  $\beta$  phase over 623K. Heat treatment in vacuum gave the same results. The higher the heating temperature, the lower the open circuit voltage and initial discharge voltage.

We have studied the effect of heating the EMD obtained by the chloride route from the Indian ore on the Li/MnO<sub>2</sub> button cell performance in combination with different concentrations of lithium perchlorate in propylene carbonate as well as mixed solvents of propylene carbonate (PC) and 1,2-dimethoxyethane (DME).

### EXPERIMENTAL

#### *Manganese dioxide*

Manganese dioxide obtained electrolytically from the Indian ore [15] has been used as the starting material. This is the gamma modification and it may contain about 5.5 percent occluded water [16]. This sample was powdered, washed free of chloride and dried. Manganese dioxide powder of less than 200 mesh size was prepared.

Portions of this sample were heated in a furnace in air for 24 hours in a silica dish at 373K, 573K, 723K and 1023K respectively. These were stored in a dry air oven at 373K. These heated EMD samples were used as cathode material in fabricating Li/MnO<sub>2</sub> button cells.

#### *Propylene carbonate*

PC (Merck Schuchart, Munich) was stored over calcium oxide for 24 hours [17]. Then it was distilled twice under calcium oxide reduced pressure in a dry box. The first and last 10 percent of the distillate were rejected to avoid steam and low boiling impurities. Afterwards, the solvent was stored over 4A° Linde molecular sieves for 48 hours. The water content estimated by Karl Fischer titrimeter was less than 30 ppm.

#### *1,2 Dimethoxy ethane*

1,2 DME obtained from Ridel de Haen, AG was distilled from lithium metal under vacuum [18], inside a dry box.

#### *Lithium perchlorate*

Lithium perchlorate (Fluka, AG) was fused in vacuum at 423K for more than 48 hours to remove any moisture it may contain [19]. This dried sample was used for preparing electrolyte solution. The calculated weights of lithium perchlorate for the various concentrations of solutions were fused separately and the fusion was repeated several times till there was no reduction in weight.

### Anode

Pure lithium metal from Foote Mineral Co., USA has been used as anode. Sizing of the anode was done inside the dry box.

### Cathode

Cathode mixtures from each EMD sample, namely those heated to 373K, 573K, 723K and 1023K respectively, were prepared by mixing 90 percent EMD and 10 percent acetylene black. Teflon was added as binder, mixed and dried. These were stored at 373°K. 200 mg from the respective cathode mix was taken and pellets were made at a pressure of 2000 kg.cm<sup>2</sup> over a nickel mesh support.

### Separator

Porous cellulose material was used as separator.

### Electrolyte solution

PC and lithium perchlorate were mixed inside the dry box in an inert atmosphere. Proportionate amounts of 1M LiClO<sub>4</sub> in DME were mixed inside the dry box for mixed solvent preparation.

The cells were fabricated and sealed in a dry box. Argon gas was flushed inside the dry box. P<sub>2</sub>O<sub>5</sub> to absorb moisture inside the box and silica to indicate the moisture inside the box were kept in separate trays. Humidity inside the box was measured by means of a humidity meter and maintained around 5%. The cell was of 20 mm dia. and 2 mm thickness.

Cells were discharged at a current of 50 μA (micro amperes). In certain cases, discharge at 100 and 200 μA (micro amperes) were also carried out. Cell potential vs time plots were constructed for each discharge experiment.

To measure the internal resistance of the cells, I-E plots were constructed and from the slope of the straight line, the resistance values were calculated. The cells were drained at different current densities and the cell voltages were measured each time using a Zenith model ZE 1501 digital multimeter.

The densities of the EMD samples were determined with a specific gravity bottle using toluene as the wetting fluid by the usual method. X-ray diffraction using Fe K -radiation was done to identify the crystal modifications.

## RESULTS AND DISCUSSION

The densities of the samples are given below:

Gamma (373K) MnO <sub>2</sub>	4.973 g/cc
MnO <sub>2</sub> heated to 573K	4.973 g/cc
MnO <sub>2</sub> heated to 723K	4.347 g/cc
MnO <sub>2</sub> heated to 1023K	4.832 g/cc

### Discharge performance

The discharge performance of a battery depends on various factors. They are, the concentrations of electrolyte, its viscosity and

conductivity, the dielectric constant of the solvent, porosity and surface area of the electrodes, rate of discharge, the temperature at which it is discharged, nature of the electrode material and the cut off voltage. We have taken care to keep the porosity and area of electrodes to be more or less constant by making pellets at a uniform pressure of 2000 kg cm<sup>-2</sup>. The porosity of the cathode pellets was calculated and the values were found to be between 62% and 67%. The cut off voltage was fixed at 2. Rate of discharge was also kept constant at 50 microamperes except in specific cases where discharges were done at 303 + 1K. Hence variations in the experiments were the concentrations of the electrolyte and the nature of the cathode material, i.e. different forms of manganese dioxide with varying occluded water content. Figs. 1-6 and Table I give the variation of discharge capacity with these two factors.

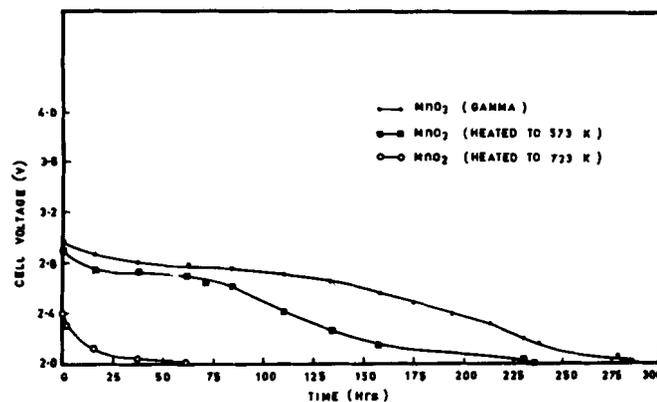


Fig.1: Discharge curves of Li cell with 0.5M PC (LiClO<sub>4</sub>) and MnO<sub>2</sub> samples, current, 50μA

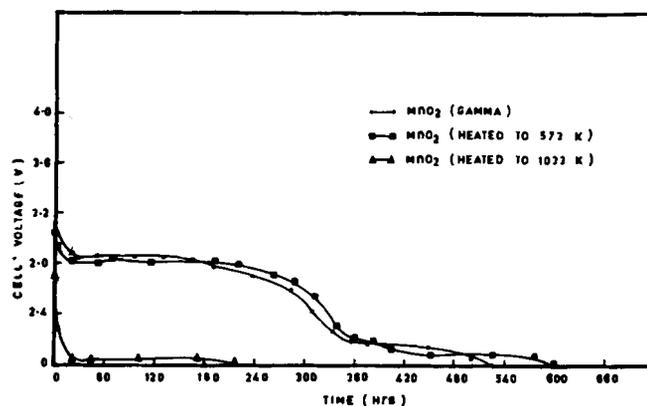


Fig.2: Discharge curves of Li cell with 1M PC (LiClO<sub>4</sub>) and MnO<sub>2</sub> samples, current 50μA

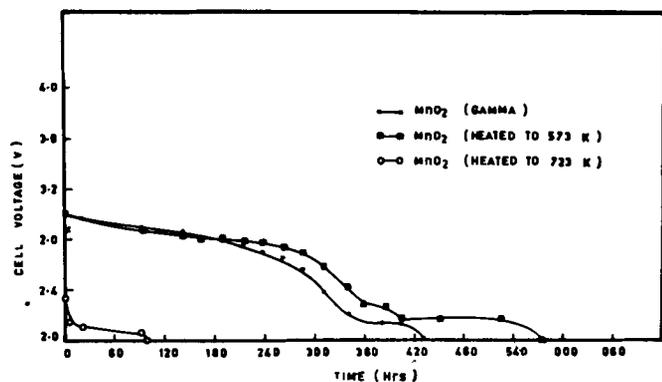


Fig.3: Discharge curves of Li cell with 1.5M PC ( $\text{LiClO}_4$ ) and  $\text{MnO}_2$  samples, current  $50\mu\text{A}$

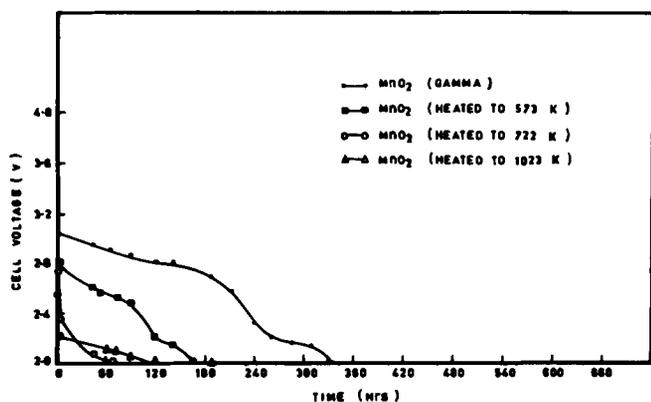


Fig.4: Discharge curves of Li cell with 2M PC ( $\text{LiClO}_4$ ) and  $\text{MnO}_2$  samples, current  $50\mu\text{A}$

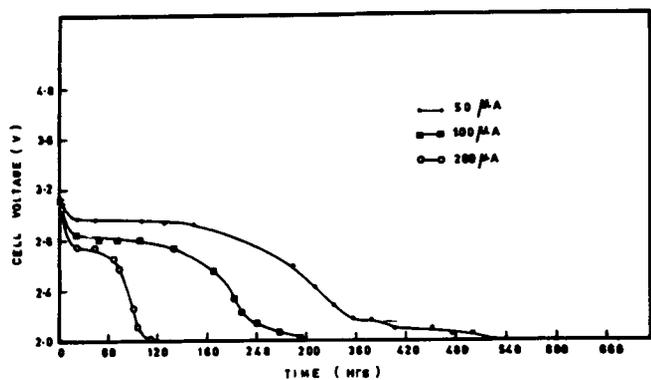


Fig.5: Discharge curves of Li/1M PC ( $\text{LiClO}_4$ )/ $\text{MnO}_2$  (gamma) cells

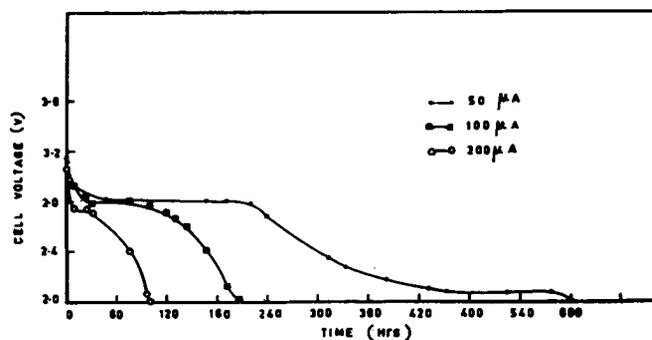


Fig.6: Discharge curves Li/1M PC ( $\text{LiClO}_4$ )/ $\text{MnO}_2$  (heated to 573K) cells

TABLE-I: Discharge performance of lithium cells with variations in  $\text{MnO}_2$  samples and concentration of PC

$\text{MnO}_2$ heating temp. K	Capacity of cells with			
	0.5 M PC ( $\text{LiClO}_4$ ) mAH	1M PC ( $\text{LiClO}_4$ ) mAH	1.5M PC ( $\text{LiClO}_4$ ) mAH	2M PC ( $\text{LiClO}_4$ ) mAH
373 (gamma)	14.2	26.3	21.6	16.8
573	12.8	30.0	28.8	8.3
723	3.0	--	4.9	3.5
1023	--	10.9	--	8.3

The conductivity of  $\text{LiClO}_4$  in PC is maximum at a concentration of one molar solution and it decreases with increasing concentration [20]. The viscosity of the solvent increases with increase in concentration and this also further changes the conductivity. From the discharge curves, it can be observed that the capacity of the cells increases upto 1MPC- $\text{LiClO}_4$  and then decreases. The capacity is less at 0.5M PC- $\text{LiClO}_4$ . For all varieties of  $\text{MnO}_2$ , we see that the maximum capacity is obtained at a concentration of 1M. As the heating temperature of  $\text{MnO}_2$  increases, the capacity decreases except at 573K. In other words, the performance of the cell increases upto 573K and then decreases. This effect is very much pronounced in the case of  $\text{MnO}_2$  heated to 1023K where the cell capacity is negligible. For the samples heated to 723K and 1023K no worthwhile discharge performance could be obtained in all concentrations. Whenever the cell capacity was too low, the discharge curves have not been given. Probably after 723K the decomposition of  $\text{MnO}_2$  takes place. As for the sample heated to 723K [12] beta  $\text{MnO}_2$  is formed at that temperature. It is well known fact that beta  $\text{MnO}_2$  has a poor battery performance in aqueous media. There is a fall of cell capacity with the heating temperature of  $\text{MnO}_2$  and the  $\text{MnO}_2$  heated to 573K gives the maximum capacity. This clearly indicates that the occluded water has got a finite influence on the performance of  $\text{MnO}_2$ .

**Internal resistance**

The simple way of determining the internal resistance of a battery is to measure the voltage of the battery at various discharge current densities. Then the voltage vs current plot is to be drawn. The slope of the curve gives the internal resistance of the battery which includes the resistance of the anode, cathode, electrolyte, separator and containers. But there are no variations in anode characteristics, separators and container in the present cases. So we can have an idea of the influence of the cathode material or electrolyte concentration on the internal resistance by varying them. It is seen from Fig. 7 and Table II that the slopes of the curves decrease with increasing concentration for cells with MnO<sub>2</sub> heated to 373K and 573K. The values are irregular as we increase the temperature.

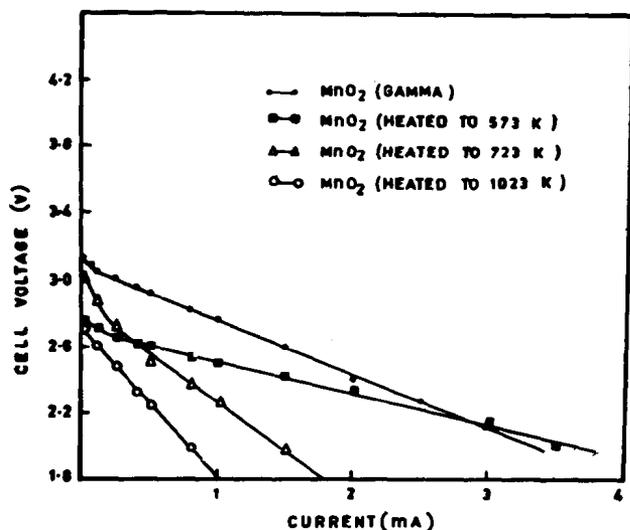


Fig. 7: I-E curves of Li cell with 1MPC (LiClO<sub>4</sub>) and MnO<sub>2</sub> samples

TABLE-II Resistance values of lithium cells with variations in MnO<sub>2</sub> samples and PC concentration

MnO <sub>2</sub> heating temp.	Int. resistance of cells with			
	0.5M PC (LiClO <sub>4</sub> ) ohms	1MPC (LiClO <sub>4</sub> ) ohms	1.5M PC (LiClO <sub>4</sub> ) ohms	2M PC (LiClO <sub>4</sub> ) ohms
373 (gamma)	400	317	378	276
573	236	184	700	1440
723	400	585	265	1236
1023	533	867	471	889

This shows that EMD heated at 373K and 573K can undergo reduction more efficiently than the other forms. They can also deliver

steady currents. The internal resistance of cells with 2M PC-LiClO<sub>4</sub> is the maximum probably due to the higher viscosity and consequent diffusion problems at this concentration.

**Effect of mixed solvents**

The performance of various crystalline modifications of MnO<sub>2</sub> in cells with reference to discharge capacity for mixtures of solvents i.e. PC and DME pf 3:1 and 1:1 was studied (Figs. 8-11). The influence of the mixed solvents was compared with that of PC.

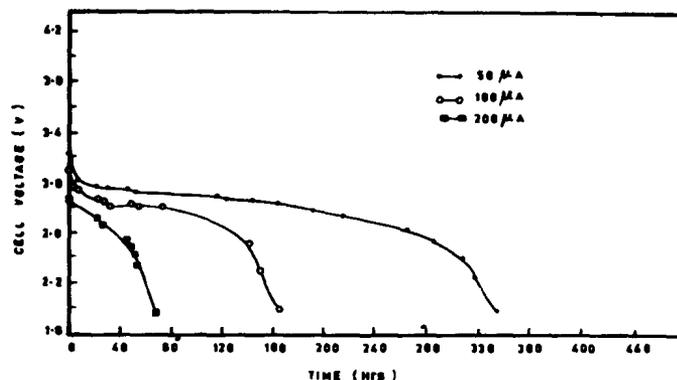


Fig. 8: Discharge curves of Li/3:1 (PC-DME) (LiClO<sub>4</sub>)/MnO<sub>2</sub> gamma cells

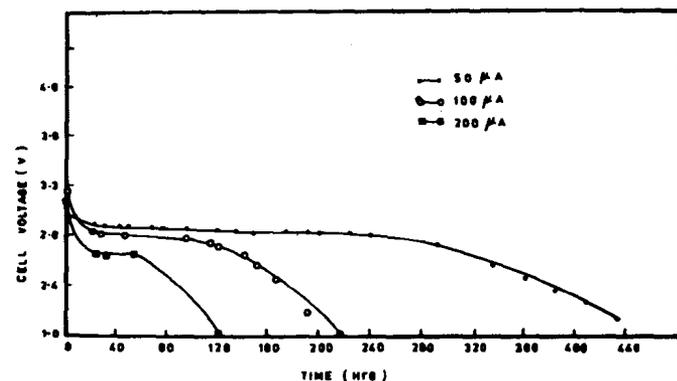


Fig. 9: Discharge curves of Li (3:1) (PC-DME) (LiClO<sub>4</sub>)/MnO<sub>2</sub> (heated to 573K) cells

By using mixed solvents, the viscosity of PC is brought down. The dielectric constant also changes.

Cell capacities fall as a result of DME addition to PC (Tables III and IV). This behaviour is reflected by the internal resistance values also. The crystallographic modifications also influence the performance of cells. The EMD samples heated to 373K and 573K alone show maximum capacity and reduction efficiency. The other

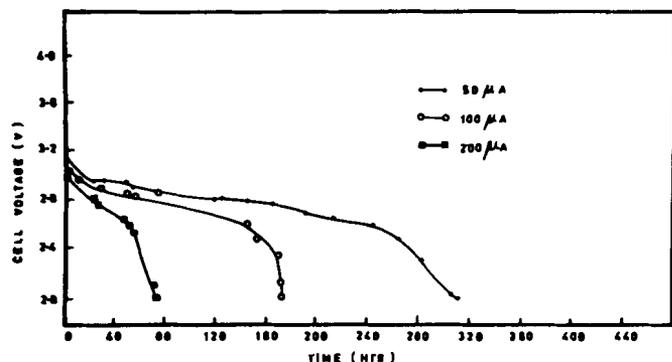


Fig.10: Discharge curves of Li/1:1 (PC-DME) (LiClO<sub>4</sub>)/MnO<sub>2</sub> (gamma) cells

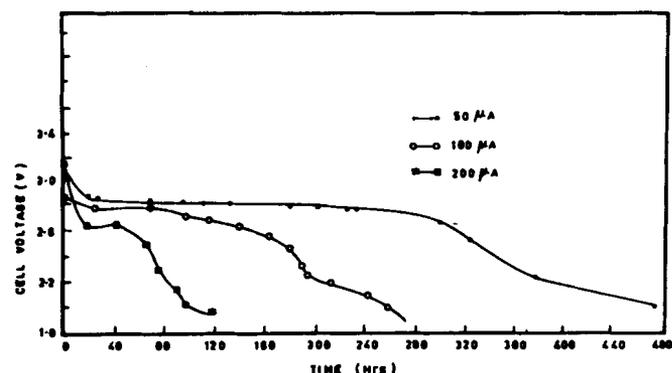


Fig.11: Discharge curves of Li/1:1 (PC-DME) (LiClO<sub>4</sub>)/MnO<sub>2</sub>(heated to 573K) cells

TABLE-III Discharge performance of lithium cells with mixed solvent and heated MnO<sub>2</sub> sample

MnO <sub>2</sub> heating temperature K	Capacity of cells	
	3:1 PC-DME (LiClO <sub>4</sub> ) mAh	1:1 PC-DME (LiClO <sub>4</sub> ) mAh
373 (gamma)	16.8	15.5
573	22.0	23.5
723	--	11.5
1023	--	--

TABLE-IV: Resistance values of lithium cells with mixed solvents and heated MnO<sub>2</sub> samples

MnO <sub>2</sub> heating temperature K	Resistance of cells with	
	3:1 PC-DME (LiClO <sub>4</sub> ) ohm	1:1 PC-DME (LiClO <sub>4</sub> ) ohm
373 (gamma)	378	462
573	453	500
723	466	444
1023	773	--

samples show negligible cell capacity and hence have not been reported.

From these, we find that the EMD heated to 573K with optimum water content is alone able to give the maximum cell capacity. This behaviour remains same in the cases of single as well as mixed solvents.

*Acknowledgement:* This paper forms a part of the thesis submitted to Banaras Hindu University by one of the authors.

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