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# CHARACTERISATION OF MANGANESE DIOXIDE FOR NONAQUEOUS LITHIUM CELLS

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## ABSTRACT

Physicochemical properties of chemically prepared $MnO_2$ were studied in detail. Li - $MnO_2$ cells were fabricated with the prepared manganese dioxide and their performance characteristics were studied. The best manganese dioxide for Li - $MnO_2$ nonaqueous cell was identified.

Key Words: Manganese dioxide, lithium cells, nonaqueous cells

## INTRODUCTION

Since its discovery [1], many types of lithium cells have been invented for commercial exploitation. Li - $SO_2$, Li - $SO_2Cl_2$, Li - $SOCl_2$, Li - $(CF)_n$, Li - CuO, Li - $FeS_2$ and Li - $MnO_2$ are a few important lithium cells used for various applications [2]. Lithium cells are in general of high energy density, long shelf life and high cell voltage [3]. They can operate at wide ranges of temperatures, depending on the solvents used [4]. Among the known lithium cells, Li - $MnO_2$ cells are the cheapest and have large commercial applications [5]. Hence, a detailed study was made by preparing $MnO_2$ under different conditions for use in the lithium cells, especially their performance characteristics during discharge processes.

Apart from natural ores [6], the important methods of preparation are, electrochemical methods [7], thermal decomposition methods [8] and precipitation methods. In the electrochemical method it is possible to deposit $MnO_2$ from $MnSO_4$ [9], $MnCl_2$ [10], or $Mn(NO_3)_2$ [11] solutions using graphite [12], Ti [13], Pg [14], Pt [15] and other anodes [16] under different conditions of pH, concentration, temperatures and current density [17]. In this paper chemical methods of preparation of $MnO_2$, [18] by thermal [19] and precipitation methods [20] are presented

## EXPERIMENTAL

The conditions of preparation of $MnO_2$ are available in detail [21]. Table I indicates the various techniques used for preparing $MnO_2$ by different chemical routes.

Table I: Methods of preparation of $MnO_2$ and allied details [8, 18, 19, 20]

| Sample | Methods of preparation of $MnO_2$ | Apparent density ($g/cm^3$) | Amount of $O_2$ in $MnO_2$ sample (mg) | Percentage of $O_2$ in $MnO_2$ sample | Internal resistance of Li.$MnO_2$ cells (ohms) |
|---|---|---|---|---|---|
| 1. | Roasting $MnCO_3$ at 400 - 450°C | 1.327 | 0.245 | 66.6 | 157 |
| 2. | Roasting $Mn(NO_3)_2$ at 250 - 270°C | 1.626 | 0.252 | 68.5 | 150 |
| 3. | Reaction of $KMnO_4$ and KI | 1.443 | 0.268 | 72.9 | 150 |
| 4. | Reaction of $MnSO_4$ and $KMnO_4$ | 1.284 | 0.267 | 72.6 | 240 |
| 5. | Reaction of $KMnO_4$ and dil HCl | 1.426 | 0.305 | 82.9 | 66 |
| 6. | Reaction of $KMnO_4$ and $H_2SO_3$ | 1.417 | 0.303 | 82.3 | 81 |
| 7. | Roasting a mixture of $MnCO_3$ and $NaHCO_3$ | 1.290 | 0.282 | 76.5 | 200 |
| 8. | Roasting $KMnO_4$ crystal at 200°C | 1.454 | 0.297 | 80.7 | 210 |
| 9. | Reaction of $MnSO_4$ and NaOH | 1.689 | 0.280 | 76.8 | 325 |
| 10. | Reaction of $KMnO_4$ and nitrotoluene | 1.871 | 0.222 | 54.9 | 115 |
| 11. | From $H_2O_2$, $NH_4OH$ and $KMnO_4$ | 1.316 | 0.237 | 64.4 | 193 |
| 12. | Reaction of $KMnO_4$ and $(NH_4)_2S_2O_8$ | 1.584 | 0.350 | 95.1 | 38 |
| 13. | Reaction of alkaline $KMnO_4$ and HCHO | 1.408 | 0.313 | 85.1 | 213 |

## a) SEM analysis

Studies were made to get the SEM analysis of various samples for a magnification of 1000 in order to understand the crystalline or amorphous character of $MnO_2$. The samples were prepared in a suitable base. The samples were embedded over a thin film of epoxy resin as a gold cup of radius 300 Å and introduced in SEM for getting the photographs.

## b) Specific gravity

The powdered samples were porous in nature. Hence, it is difficult to get the true density of the samples. As a battery cathode material, density of $MnO_2$ plays a very important role in its performance. For a given volume more of $MnO_2$ can be packed if the density is high. The apparent density of the samples were determined using pycnometric method [22]. The results of experiments were calculated using the equation

$$\frac{W_3 - W_1}{(W_4 - W_1) - (W_2 - W_1)} = \text{apparent density}$$

where $W_1$ = weight of the empty pycnometer

$W_2$ = weight of pycnometer with water

$W_3$ = weight of sample + pycnometer

$W_4$ = weight of sample and water inside the pycnometer

## c) Estimation of $O_2$ in $MnO_2$

The depolarisation action of $MnO_2$ largely depends on the non-stoichiometric property of the prepared sample. The available oxygen content in $MnO_2$ has been estimated along with Mn content using potentiometric titration method [23].

## d) Cathodic polarisation of $MnO_2$ under galvanostatic conditions

*i) Cell:* A three electrode cell was used for this purpose with a platinum foil as auxiliary electrode and a lithium electrode as a reference electrode. Manganese dioxide powder of −200 mesh was mixed with 10 % acetylene black and 1 % polyethylene binder and was heated to 110° C for four hours. This mixture was spread over a nickel mesh and was pelletised at a pressure of 7000 kg/cm$^2$. From this pellet suitable leads were taken for measurements.

*ii) Electrolyte:* Propylene carbonate (PC) was dried over anhydrous CaO and purified by vacuum distillation at 3 - 4 mm of Hg at 200° C and dried over 4 Å molecular sieves. This sample was further purified with lithium powder, discarding first 10 % of the distillate. The water content in the solvent was estimated by automatic Karl Fischer Titrimeter. 1 : 2 dimethoxyethane (DME) was dried over CaO and distilled at 80° C under vacuum. Lithium perchlorate ($LiClO_4.H_2O$) was dried in a vacuum furnace at 120° C for 48 hours.

*iii) Solution:* The electrolytes 1M $LiClO_4$ in PC and 1M $LiClO_4$ in DME were prepared in a dry box under argon atmosphere.

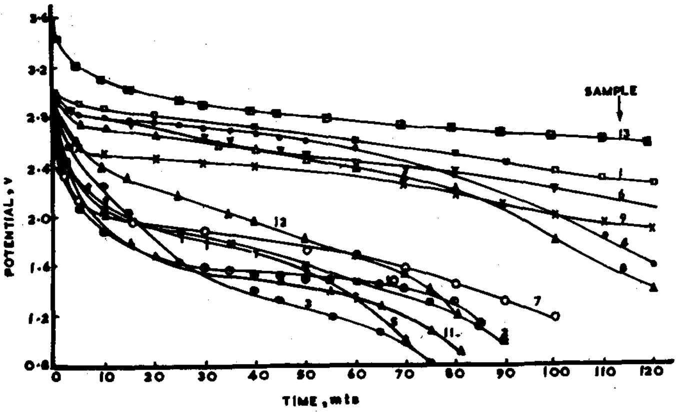


Fig 1: Cathodic polarisation studies of $MnO_2$ (4 mA)

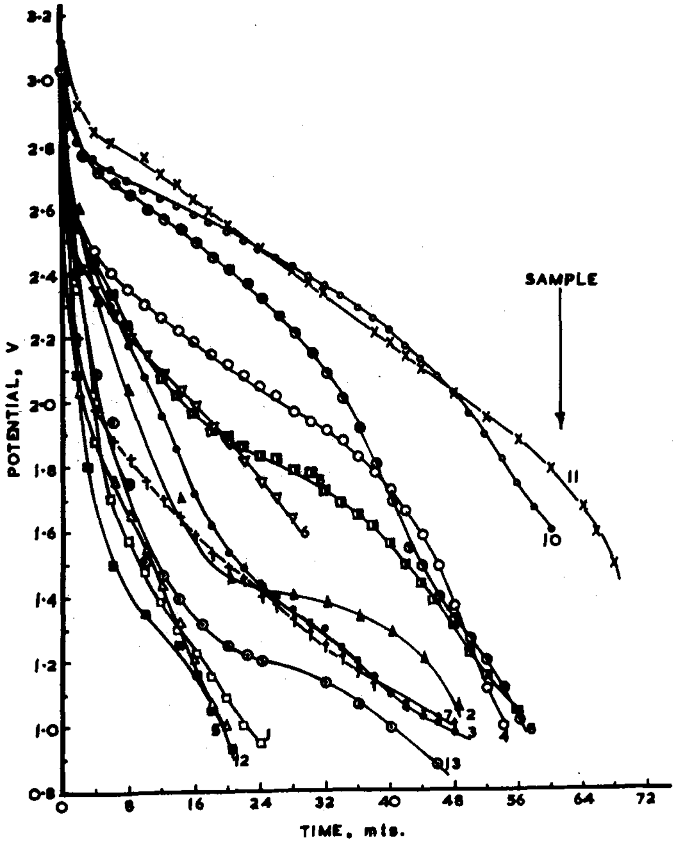


Fig 2: Cathodic polarisation studies of $MnO_2$ (8 mA)

*iv) Galvanostatic method:* A cell was assembled in the dry box. A current of 4 mA (Fig. 1) was passed between the Pt and $MnO_2$ electrodes and the potential of the $MnO_2$ electrode was sensed with lithium reference, electrode with the aid of a printing Voltmeter. The experiments were repeated with 8 mA current (Fig. 2).

*v) I-E Characteristics:* A lithium - $MnO_2$ button cell was assembled using lithium metal, a cathode mix containing $MnO_2$, a paper separator, and a solution containing 1M $LiClO_4$ and PC + DME mixture. The fabricated cell was subjected to different rates of discharge of current by measuring the potentials with time (Fig. 3).

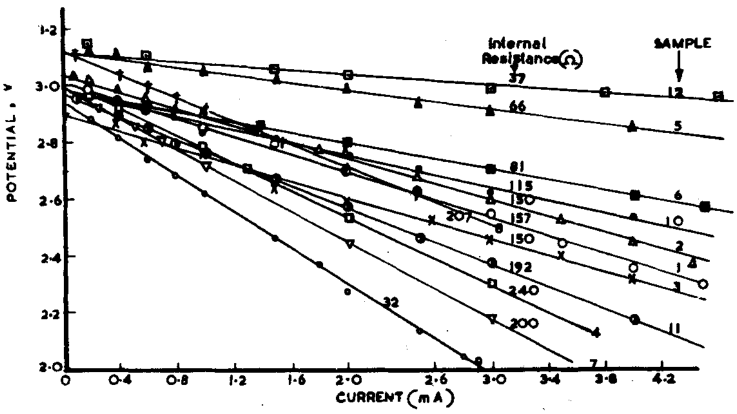


Fig 3: I-E characteristic of Li-$MnO_2$ button cell

## RESULTS AND DISCUSSION

Manganese dioxide has been used as a successful cathode/depolariser in neutral [24] alkaline [25] and nonaqueous media [26]. The performance characteristics of manganese dioxide depends on various factors like method of preparation, apparent density, oxygen content and morphology. All the samples prepared as in Table I were subjected to physicochemical and electrochemical studies. The morphological studies with SEM analysis reveal that most of the samples have white spots showing less conducting portion, some develop crystal structure (samples 2, 3, 4, 12) and the rest are amorphous in nature. Hence, the polarisation behaviour of the manganese dioxide vary from sample to sample. The apparent density of the samples varies from 1.28 to 1.87 depending on the method of preparation. Since apparent density is a factor which contributes to the content of the cathodic depolariser in a given volume its amount plays very important role in the performance of the battery.

A thorough scrutiny of the results obtained show that the percentage of $MnO_2$ in the various samples varies according to the method of preparation. The $MnO_2$ content is found to be very small in the case of the sample prepared by the reduction of $KMnO_4$ with nitrotoluene. However, the apparent density of this sample is the highest. Similarly the apparent density of the sample 2 is high but $MnO_2$ content is found to be low. In all other samples the $MnO_2$ containing $O_2$ is above 80%. In all these samples it is observed that the $O_2$ content is found to be low due to the fact that the conversion of $MnO_2$ is partial and products like MnO, $Mn_2O_3$ and $Mn_3O_4$ will be formed when $Mn(OH)_2$, $Mn(BO_3)_2$ and $MnCO_3$ are heated.

Manganese dioxide was cathodically polarised under galvanostatic conditions and the nature of the polarisation curves were studied in detail at 4 mA and 8 mA currents in PC + DME mixture containing $LiClO_4$. The samples 6, 12 and 13 show uniform variation of potential with time. Therefore these samples are the best depolarisers in Li - $MnO_2$ cells. It is also notice that these samples have fairly good apparent density and high oxygen content. The other samples cannot give better efficiency of reduction of $MnO_2$ due to the formation of suboxides. The polarisations were carried at 8 mA current and the I - t curves show a steep fall showing that the cells cannot deliver high currents.

## CONCLUSION

The sample of $MnO_2$ prepared from $MnSO_4$ + $(NH_4)_2S_2O_8$ or reduction of $KMnO_4$ with HCHO or $H_2SO_3$ shows satisfactory performance as a depolariser in nonaqueous Li - $MnO_2$ cells.

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